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INFRA-RED ABSORPTION SPECTRA, II.

LIQUIDS AND SOLIDS.

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IN the complete account of this work a chapter is devoted to a detailed discussion of each compound studied. In this paper it will be impossible to include more than a brief outline of the more important relations found. For the substances mentioned here the principal results are put in convenient form for reference in Figs. 7, 10 and 11. The lines in these plots represent, in height and in position, the principle absorption bands of some of the compounds studied.

In general the transmission spectrum of each compound shows some interesting property which cannot be correlated with that of a different compound. For example, Friedel,[1] using Tyndall's method of total absorption, found that methyl and ethyl iodide are far more transparent than nitrogen compounds. It will be noticed, Fig. 10, that these iodides have large absorption bands in the region of $10\,\mu$ where the radiation from a black body is very weak. They are quite transparent in the region of $2\,\mu$ where the black body radiation is strong. Consequently, in measuring their total transmission, the great transparency found by Friedel is not due to the *lack* of absorption bands but to the fact that the absorption bands lie beyond the region of the black body radiation. A more conspicuous example of the reverse effect was found by Drew[2] in his work on vacuum tube

[1] Friedel, Ann. der Phys., 55, p. 453, 1895.

[2] Drew, PHYS. REV., Vol. XVII., p. 321, 1903.

radiation. He used a cell of CS_2 as an absorbing medium, and found it as opaque as water. This is due to the fact that nearly all of the radiation from the tube is concentrated in a strong emission band at 4.75 μ, which coincides with a strong absorption band of CS_2 at 4.7 μ.

Benzonitrile, C_6H_5CN, is an excellent example of a compound having no strong absorption bands until we arrive at 13.25 μ. This is also the only compound studied which has a series of *small*, narrow, absorption bands extending throughout the spectrum [Fig. 10.]

Eucalyptol, $C_{10}H_{18}O$, is the only compound studied which has a large band of general absorption, extending from 7 μ to 14 μ, beyond which point the substance becomes more transparent the farther one penetrates the infra-red — to 15 μ.

The Spectrum from .8 μ to 2.75 μ.

Puccianti,[1] using a quartz prism and a radiometer, explored the transmission spectra of sixteen liquid compounds. His curves show that all compounds, the molecules of which contain carbon combined directly with hydrogen, present a maximum absorption at 1.71 μ, while all the benzene derivatives have two other maxima in common at 2.18 μ and 2.49 μ. The three alcohols examined by him have a band in common at 2.05 μ.

The results obtained by him seemed so unusual that a continuation of the work was deemed necessary. Accordingly, eighteen new compounds were examined As a whole the results obtained are in excellent agreement with those of Puccianti. The band found by him at 1.71 μ was located at 1.68 μ to 1.7 μ, depending upon the compound. It was found in *all* the carbohydrates studied. The slight shift does not appear to be due to shifting of the apparatus, and is to be found in the more complex compounds, just as is true farther in the infra-red. The 2.18 μ and the 2.49 μ bands of benzene derivatives are also sometimes slightly shifted in the complex derivatives like pinene, eucalyptol, and safrol. As a whole the curves form an interesting study by themselves.

General Discussion of the Spectra.

Since the object of this investigation was to determine the effect of molecular weight, of chemical structure, etc., upon the absorp-

[1] Puccianti, Nuovo Cimento, II., p. 241, 1900.

tion of heat waves, it will simplify matters to discuss each of these topics separately.

A few transmission curves are included to give the reader an idea of their general appearance.

Effect of Structure. — In order to learn what effect a group of atoms in a molecule has upon infra-red absorption spectra, the most logical procedure is to study isomeric compounds in order to determine fully that the phenomenon is intramolecular, and after that attempt to locate the particular group of atoms suspected of causing the disturbance. In many cases the spectra of isomers is very similar until we extend our observations far into the infra-red. The total number studied is so large and varied, however, while the

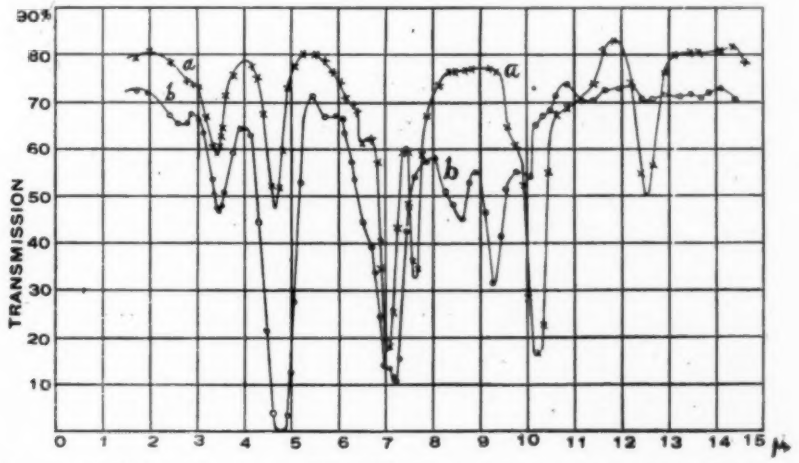

Fig. 5. Methyl Sulphocyanate, CH_3-SCN; Curve *b*, Methyl Mustard Oil, CH_3NCS; $t = .01$ mm.

change in the spectra of a pair of isomers is so marked, that there can be no question that this is due to structure rather than impurities. In aniline, $C_6H_5NH_2$, and its isomer, picoline, $C_6H_4N(CH_3)$, Fig. 7, the effect of structure is very marked. The benzene band at 3.25 μ, found in aniline, is entirely obliterated by the one at 3.35 μ in picoline, while in the spectrum of picoline only one band, at 10 μ, is in common with that of aniline. In the sulphocyanites, R-SCN, and the mustard oils, R-NCS, the effect of structure is still more pronounced. The small band of the sulphocyanates at 4.68 μ is com-

pletely outclassed by the 4.78 μ band in the mustard oils, Fig. 5. As the band occurring from 3 to 3.4 μ is a characteristic of carbohydrates so is this band a characteristic of the mustard oils. Of all compounds studied, the mustard oils are unique in having an enormous absorption band in the region of shorter wave-lengths, this side of 5 μ. In CS_2 the first strong band occurs at about 6.7 μ, in methyl iodide at 11.35 μ, and in carbon tetrachloride at 13 μ.

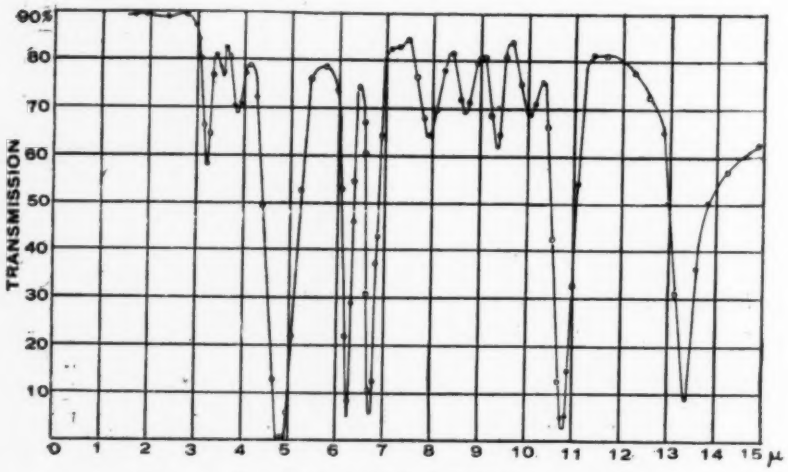

Fig. 6. Phenyl Mustard Oil, C_6H_5NCS; $t = .01$ mm.

In allyl mustard oil, C_3H_5NCS, using the large spectrometer, this band was found to be complex, being opaque from 4.5 μ to 4.9 μ, with the maximum located at about 4.8 μ. Phenyl mustard oil, C_6H_5NCS, Fig. 6, is still more interesting since it contains the 3.25 μ band as well as several others belonging to benzene and has, in addition, this strong band of the mustard oils, located at 4.8 μ, just as though the CH and the CS ion were vibrating side by side but independently of each other.

Other isomers like pinene and limonene, $C_{10}H_{14}$, have a great similarity until we arrive at 10 μ, while the caproic acids, Fig. 7, are identical to 6 μ and begin to show dissimilarity at 8 μ. Probably the most evident example of the influence of structure is in the aliphatic or chain linked compounds, like octane, and the carbocyclic, or ring compounds, like benzene. If we consider simply the number of atoms in the molecule then the benzene series, C_nH_{2n-6}, can be

classed with the chain series, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n+2}. Hence, reasoning from the fact that, in the three groups of chains compounds studied, all the conspicuous bands occur in common, one would, expect at least a few of the bands to occur in the benzene, C_nH_{2n-6}, series. But no such coincidence occurs; and only after the substitution of CH_3 groups for H atoms in benzene do we find bands, *e. g.*, 3·43 μ, in common with those of the chain compounds. If, then, we had no knowledge of organic chemistry, the evidence presented here would be sufficient to conclude that we are dealing with two distinct classes of compounds.

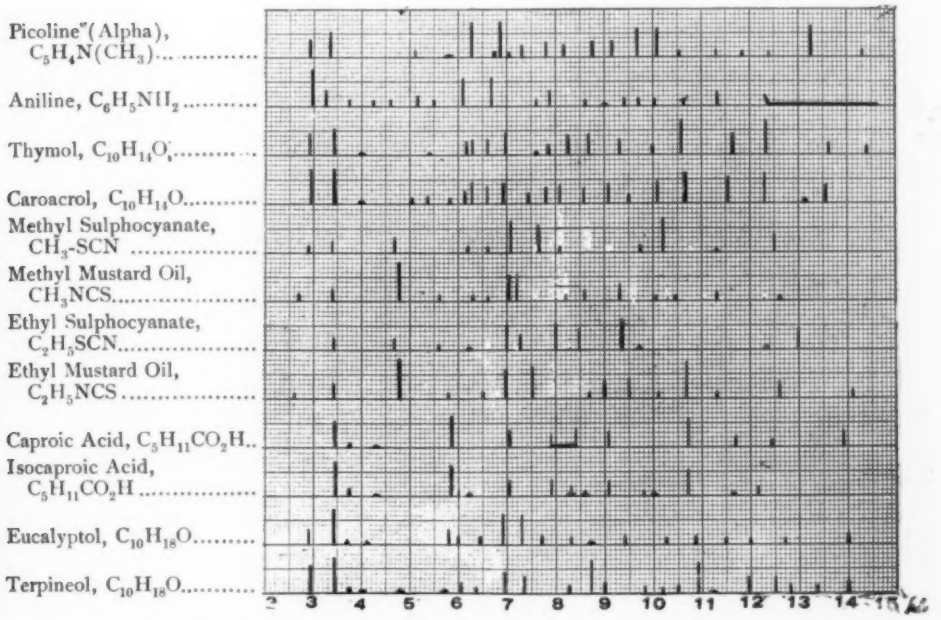

Fig. 7. Isomeric compounds illustrating effect of structure upon absorption. Height of lines indicates depth of bands.

Thymol and carvacrol, Fig. 7, methyl ether and ethyl alcohol, eucalyptol and terpineol, and the three isomeric xylenes are additional examples showing very clearly the marked influence of the arrangement of the chemical atom in the molecule upon the resulting absorption spectrum. In the xylenes the bands occur in groups; while the location of the maximum of each group seems to occur

in the order *para*, *meta*, *ortho*, with increase in wave-length, Fig. 10. In thymol and carvacrol the change in the spectra begins to manifest itself at 5 μ and 6 μ while from 9 μ to 14 μ the spectrum is entirely rearranged. In methyl ether and ethyl alcohol we have the most marked change in the location of the absorption bands, which is noticeable throughout the whole spectrum.

As a whole, the present investigation substantiates the conclusions of Julius (*loc. cit.*) of the influence of structure upon absorption spectra.

Effect of Molecular Weight. — In the present work the results agree with that of Krüss,[1] in so far as it seems permissible to assume that the occurrence of a certain conspicuous absorption band in a different place is a real shift. The benzene derivatives are the most noticeable example. In benzene, C_6H_6, the maximum occurs at 3.25 μ and is shifted to 3.3 μ in toluene, $C_6H_5CH_3$, to 3.38 μ in the xylenes, $C_6H_4(CH_3)_2$, and to 3.4 μ in mesitylene, $C_6H_3(CH_3)_3$ [Fig. 10]. In other words by substituting three CH_3 groups for an H atom we have shifted the maximum from 3.25 μ to 3.4 μ. Of all the compounds studied, excepting the gases, this is the only example where such a supposed shifting occurs. For a shift toward the *shorter* wave-lengths, certain derivatives of benzene containing nitrogen are the most conspicuous, just as found by Krüss. In aniline, $C_6H_5NH_2$, we find the benzene band almost obliterated and the minimum shifted to 2.97 μ, just as in ammonia, while in picoline we have the ammonia band at 2.92 μ and a second band at 3.35 μ. It is to be noticed that in the xylenes and pyridine the benzene band at 3.25 μ has not been entirely obliterated, just as though there were two resonating ions, benzene and CH_3, vibrating side by side. This is more evident in xylidine and the mustard oils.

In xylidine, $C_6H_3(CH_3)_2NH_2$, Fig. 10, which has an NH_2 group and two CH_3 groups, we have the respective bands *found in ammonia*, at 2.95 μ, and in compounds predominating in CH_3 groups at 3.43 μ. The structural formula of aniline indicates that in the original benzene ring an H atom has been replaced by an NH_2 group, while in picoline we have the double benzene ring containing an N atom and a CH_3 group. The absorption spectra support this theory for

[1] Krüss, Zeit. f. Phys. Chem., 2, 312, 1888.

in the aniline spectrum we have the original benzene band at 3.25 μ and the NH_2 band found in ammonia, xylidine, etc., while in picoline we have the benzene band obliterated and the CH_3 band substituted. The latter band occurs at 3.35 μ, the mean of 3.25 μ and 3.43 μ instead of 3.43 μ. Can we say then that there is a *real shifting* of the 3.38 μ band in the xylenes? It must be remembered that we are integrating through a complex band, which with ordinary dispersion cannot be resolved with a bolometer or a radiometer. Hence, when we find the maximum shifted to 3.3 μ in anisol and to 3.4 μ in mesitylene, and find the separate bands in aniline, etc., it is a difficult matter to decide whether we have a true shifting, or whether we have simply determined the center of gravity of the several bands. An excellent example of this type is thymol, which melts at 44°. The solid film gave a deep band at 3.2 μ. In the melted condition the film was more homogeneous, and two bands were found, at 2.92 μ and 3.42 μ respectively, instead of the mean at 3.2 μ. Other examples have been observed when the layer of liquid under examination was too thick.

There are other bands farther out in the infra-red which shift back and forth just as noted above, but here the original benzene bands are more numerous. The most noticeable ones are those of the methyl sulphocyanate at 7.06 μ and 7.61 μ which occur at 6.91 μ and 7.27 μ in ethyl sulphocynate. However, in all the benzene derivatives studied the occurrence of an apparently new band in the derivative does not always seem to be a *new* band, but simply that the derivative has brought about a condition within the molecule such that the original resonating ion has a greater freedom.

In gases there is a more definite shifting of the absorption band lying between 3 and 3.5 μ, as shown in Table I.

TABLE I.

Gases.	Maxima.	Maxima.
Acetylene, C_2H_2	3.08 μ	7.38 μ
Ethylene, C_2H_4	3.28	6.98
Ethane, C_2H_6	3.39	6.85
Butane, C_4H_{10}	3.42	6.85
Methyl ether, $(CH_3)_2O$	3.45	6.88
Ethyl ether, $(C_2H_5)_2O$	3.45	7.00
Methane, CH_4	3.31	7.70

In the region at 6.8 μ to 7.0 μ there is a similar shifting but there is less regularity in the positions of the bands. Ångström[1] has shown that the occurrence of the CO_2 band at 4.28 μ and the CO band at 4.59 μ invalidates the assumption that the position of an absorption band depends upon molecular weight. Ransohoff's[2] work shows that for the alcohols there is no shifting with increase in molecular weight.

Within the experimental errors of observation Puccianti's work for the region of 1.71 μ shows no shifting of the maximum of an absorption band.

In all my work of the different compounds like methyl and ethyl iodide, -nitrate, -cyanide, -aniline, etc., no shifting could be detected.

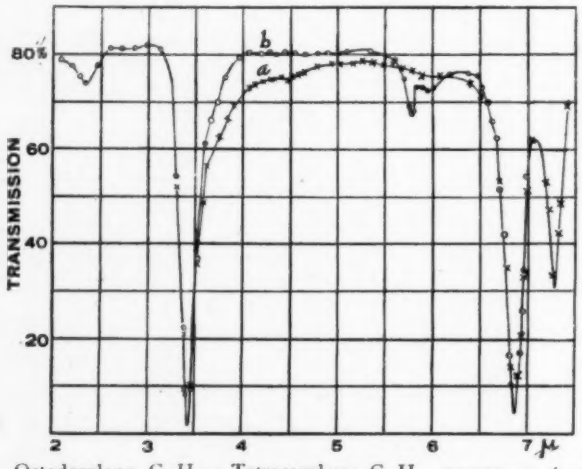

Fig. 8. Octadecylene, $C_{18}H_{36}$; Tetracosylene, $C_{24}H_{48}$, xxxxxxx; $l = .01$ mm.

To make this test conclusive for the marked band at 3.43 μ this region was examined for both compounds (methel and ethyl) before setting the spectrometer for another part of the spectrum. In this manner a slight shift noticed in methyl and ethyl iodide which had been examined on different dates, several months intervening, was found not to exist, showing an instrumental error. This method of testing a series of compounds at one region of the spectrum on the same day is the only way to be certain of slight differences in wave-

[1] Ångström, loc. cit.

[2] Ransohoff, Inaug. Diss., Berlin, 1896.

length. Through the generosity of Professor C. F. Mabery, who presented me with twenty-five very pure distillates of petroleum belonging to the series C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n+2} a final test was applied to this perplexing question. The absorption spectra of two of these, octadecylene, $C_{18}H_{36}$, boiling point 118°–120°, and tetracosylene, $C_{24}H_{48}$, solid, boiling point 274°–276° (50 mm.), are given in Fig. 8, for which the large spectrometer was used. Curve *a* is $C_{18}H_{36}$.

In these, as well as the intermediate ones, no shifting could be detected, although the greatest efforts were made to do so. This was not a little surprising for according to the measurements on the alcohols by Schönn[1] in the visible spectrum a shift for this greater number of CH_2 groups should have occurred. For, even if we assume that the shifting is least for the infra-red and increases as we approach the ultra-violet, unless the total shift, for this increase of 16 CH_2 groups (octane $C_8H_{18} = CH_3(CH_2)_6CH_3$, tetracosane $C_{24}H_{50} = CH_3(CH_2)_{22}CH_3$), is less than .01 μ it is safe to assume that no shifting occurred. At least, if there is a shifting, it is less than .01 μ which is much smaller than one would anticipate from observations in other regions of the spectrum.

A shift of .01 μ at 3.43 μ is 8″ of arc on the spectrometer circle, and at 6.86 μ it is 12″ of arc, so that it would have been impossible to escape detection — especially in the case of such deep, well defined bands as these. It is to be remembered that a separate examination was made of the 3.43 μ and the 6.86 μ bands for $C_{18}H_{36}$ and $C_{24}H_{48}$, using the large spectrometer [Fig. 8]. This was done to avoid the possibility of a shifting while examining the whole spectrum. Only seven spectrometer settings, at intervals of 1′, were made for each of these two bands. First, the zero of the instrument was determined by means of the sodium flame, then the 3.43 μ region was examined for $C_{18}H_{36}$, the examination being from *right* to *left*, say; the $C_{24}H_{48}$ was then examined going backwards, from *left* to *right*, and then from *right* to *left*, after which the zero was again tested by means of the sodium flame. The 6.86 μ band was examined in the same manner, but in neither case could a shifting of the band be detected, as will be noticed in the curves, Fig. 8. These two bands are so sharp that if a shifting of .01 μ

[1] Schönn, Ann. der Phys., 6, p. 267, 1879.

had occurred it could have been detected. It is true that these bands vary by .01 μ for some of the other oils, but that is to be ascribed to errors in reading the curves as well as to the fact that the small spectrometer was used, and that in general it was not practicable to make the examinations in the manner just described. A shift of .02 μ was easily observed in the bands of xylene and mesitylene at 3.4 μ.

An interesting fact to be noticed in this connection is that *all* the prominent lines found in the two oils just mentioned are present in all the petroleum oils studied, as well as in many other compounds, like myricyl alcohol, piperidine, etc. For a large dispersion the transparent region at 4 μ to 6 μ remains so for some oils, while in others numerous small bands were found [see Fig. 8].

The difference between the spectra of the oils (aliphatic series) and the benzene spectrum (carbocylic series) has been noticed under the question of structure. The benzene spectrum as well as that of its methyl derivatives is banded, "channeled," *i. e.*, the lines occur in groups just as Pauer[1] found in the ultra-violet [see Fig. 10]. He found the bands of the benzene spectrum, which extend from .267 μ to .235 μ, condensed and shifted toward the visible spectrum for toluene, the xylenes, aniline, etc., and considered it due to increase in molecular weight. If we consider the center of gravity of the benzene bands at about .245 μ and that of the methyl derivatives at about .267 μ this shift amounts to .02 μ while for analine it is about .05 μ.

As a whole there is no evidence of a real shifting of the maximum with increase in molecular weight, if we except the xylenes and the gases mentioned, for the region at 3.1 μ to 3.5 μ, which is not resolved for most compounds. The condition is similar to that in Kayser and Runge's work on the emission spectrum of the elements, in which they observed that, for the alkali metals, the violet lines shifted toward the longer wave-lengths with increase in atomic weight; but they could not establish[2] this relation for all the elements.

Effect of Temperature. — There is little to be said on this subject

[1] Pauer, Ann. der Phys., 61, p. 363, 1897.
[2] Kayser's Spectroscopie, II., p. 591.

for no effect due to rise of temperature of about 20° has been observed. As already mentioned, the absorption cell was between the spectrometer slit and the Nernst heater, with the double sheet iron asbestus shutter intervening. It was necessary to have the heater close to avoid loss of radiation. Consequently, in the course of a series of observations, lasting four hours, the cell would unavoidably become warmer, due principally to the raising of the shutter in making observations. This was first noticed in thymol, melting point 44°, which in the course of examination as a solid film became a liquid. It is quite crystalline in a solid film, hence more opaque due to scattering of the rays, so that it became more transparent on melting. This is the only compound found to behave thus.

It was an easy matter to repeat the observations on several sharp absorption bands, after finishing the exploration of the whole spectrum, to see whether the transparency remained the same as in the beginning; and in *no case* was there a change observable excepting for the solid thymol just mentioned.

This fact that the cell became warmer was utilized in examining several compounds with low melting points, *e. g.*, phenol and menthol, in their liquid state. It was only necessary to melt them before placing them upon the spectrometer arm, then keep the shutter raised longer than usual. This made possible the examination of several solid compounds which would have been too opaque because of their scattering effect.

The Effect of Certain Characteristic Groups of Atoms. — Having shown that infra-red absorption spectra depend upon the internal structure of the molecule and that their maxima are not influenced by molecular weight (of the molecule as a whole, *e. g.*, the petroleum distillates) the next step is to determine, if possible, what groups of atoms, or ions, have the power of absorbing heat waves. This is of considerable importance since many recorded phenomena have been credited to "the resonance[1] of the

[1] Marx, Potentialfall und Dissociation in Flammengasen, Drude's Ann., 2, p. 795, 1900 (also on Electromagnetic Resonance, Wied. Ann., 66, p. 600, 1898). After a lengthy discussion concludes that although it is a plausible assumption it has not been proven that electrolytic dissociation in a flame depends upon the effect of the electromagnetic resonance of the OH ion upon the infra-red radiation.

OH ion in the molecule." Aschkinass [1] found the absorption bands of water at the wave-lengths 1.51 μ, 3.06 μ and 6.1 μ. Although he says little about the sequence of the maxima subsequent writers have laid considerable stress upon it, as showing harmonics, *i. e.*, electromagnetic resonance. Marx [2] in finding the dielectric constants of water for electrical waves finds a double harmonic relation for the electrical region. Ransohoff (*loc. cit.*) studied six alcohols and found the bands harmonic at 1.71 μ (3.0 μ) and 3.43 μ, although the alcohols were "chemically pure" that is a different question from the one of having them "water free," which he does not consider, and the 3.0 μ and 6.06 μ bands may be due to water. The higher alcohols, like glycerine, even if they could be freed from water are so hydroscopic that they are difficult to investigate. In

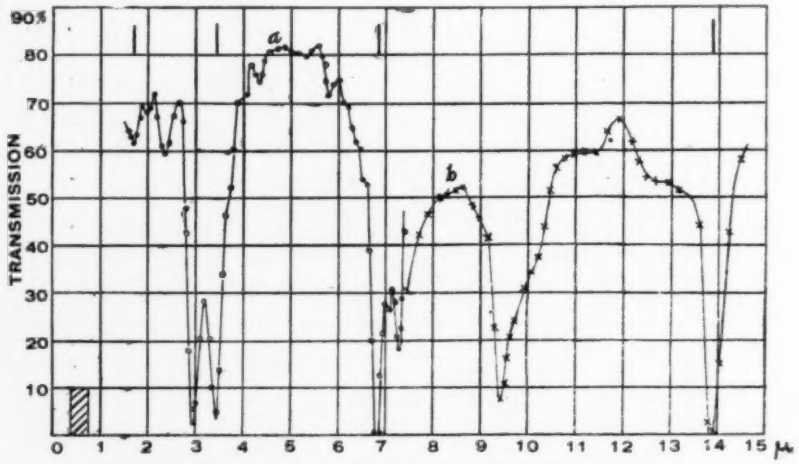

Fig. 9. Myricyl Alcohol, $C_{30}H_{61}OH$; a = large spectrometer.

the present work alcohols were not investigated because of their great opacity beyond 7 μ as well as on account of the difficulty in freeing them from water. Only one alcohol was studied, viz., myricyl, $C_{30}H_{61}OH$, which is a solid obtained from beeswax [Fig. 9]. Its maxima occur at 1.71 μ, 2.95 μ, 3.43 μ and 5.8 μ. The water bands were found at 2.95 μ and 6.0 μ so that if the alcohol bands are due to the OH group then one would expect the 5.8 μ band to coincide with that of water, at 6.0 μ.

[1] Aschkinass, Ann. der Phys., 55, p. 401, 1895.
[2] Marx, *l. c.*

TABLE II.

Compounds.	Maxima.	Remarks.
Water, HOH	2.95 μ	Depth is 70 per cent. as found with larger spectrometer.
Thymol, Carvacrol } $C_{10}H_{13}OH$	2.92	
Eugenol, $C_{10}H_{11}O\text{-}OH$	2.89	
Methyl salicylate, $CH_3OOC\text{-}C_6H_4OH$	3.1	Depth 70 per cent., probably the mean of the 3.25 μ and 2.95 μ bands.
Menthol, $C_{10}H_{19}OH$	3.0	50 per cent., comparison spectrum of H_2O at 2.95.
Phenol, C_6H_5OH	2.97	60 per cent.
Ammonia, NH_3	2.92	30 per cent.
Pyridine, C_5H_5N	2.95	30 per cent.
Picoline, $C_5H_4N(CH_3)$	2.92	Band shallow, 3 per cent.
Piperidine, $C_5H_{11}N$	3.00	30 per cent.
Aniline, $C_6H_5NH_2$	2.97	70 per cent., very sharp.
Xylidine, $C_6H_3(CH_3)_2NH_2$	2.95	50 per cent.
Pyrrol, $C_4H_4(NH)$	2.95	70 per cent.
Eucalyptol } $C_{10}H_{18}O$	2.90	30 per cent., oxide, does not contain an OH group.
Terpineol } $C_{10}H_{18}O$	2.93	30 per cent.

In Table II. it will be noticed that ammonia also has a band near that of water, and at a slightly less wave-length. Considerable time was spent in showing that it is not due to water vapor. The gas was fractionally liquefied and distilled and then placed in a gas pipette containing freshly heated calcium oxide over mercury, for eight days. At the end of this time the absorption band coincided exactly with the one previously found showing that the band is characteristic of ammonia. Furthermore, it will be noticed that the compounds containing the amido, NH_2, group and certain ones containing nitrogen have a characteristic band in this region. These compounds were dried with potassium carbonate which would have removed traces of water. Other compounds like the aldehydes and fatty acids *do not* show this band. Commercial ethyl ether contains about 3 per cent. of water, but there is only a slight depression in the absorption curve at 2.95 μ. The fatty acids, *e. g.*, caproic stearic, etc., are of interest, because they have no band at 2.95 μ. In electrolysis the alcohols are separated into ethyl and OH ions

while in the fatty acids instead of the OH ion we have simply an H ion. Hence, reasoning from this analogy one would not expect a band at 2.95 μ for the fatty acids. In the other compounds having an OH group, *e. g.*, eugenol, thymol, menthol and phenol, strong bands are to be found shifting from 2.87 μ to 3.0 μ. They show *no* bands at 6 μ. Can we assume then that the bands at 2.9 μ to 3.0 μ are due to OH? The evidence is not very favorable.

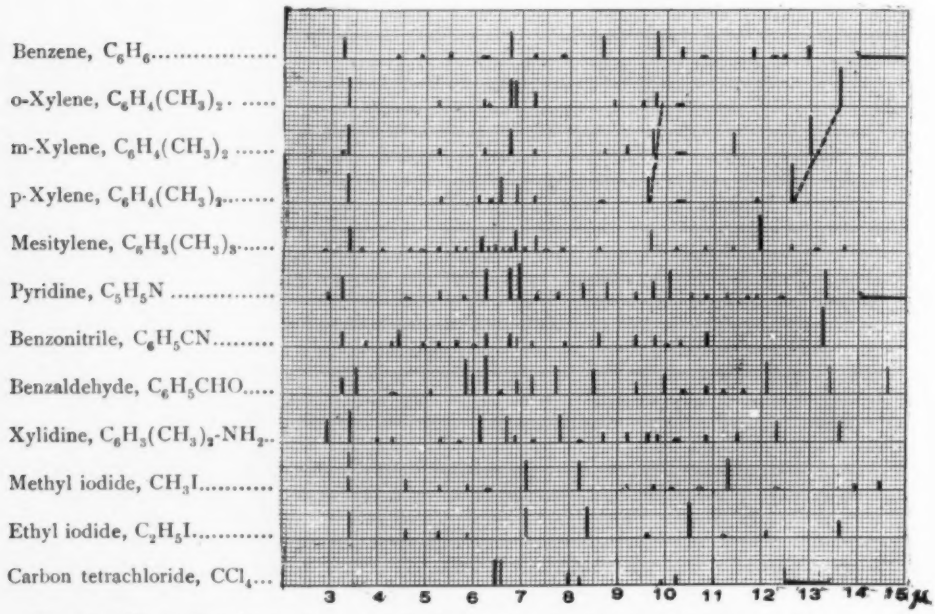

Fig. 10. Illustrating the persistence of the benzene bands at 3.25 μ and 6.75 μ in the spectra of its derivatives.

Considering the bands of ammonia and of the compounds containing NH_2, or certain ones containing nitrogen, the coincidence appears to be somewhat accidental. Farther in the infra-red we have numerous cases of the coincidence of absorption bands.

As a whole the most definite conclusion we can draw, at present, is that the alcohols have a characteristic band at about 2.95 μ just as the band at 4.78 μ is characteristic of the mustard oils.

The CH_3 group of atoms is probably the most important to be considered but only a few cases can be noticed here. The most noticeable effect is in benzene derivatives [Fig. 10]. It was shown

under the discussion of the effect of structure that the benzene group, C_6H_6, although it appears as a series C_nH_{2n-6} is entirely different from the chain compounds like C_nH_{2n-2}, etc. But a substitution of several CH_3 groups completely absorbs the 3.25 μ benzene band, and the 3.43 μ band, characteristic of all compounds containing CH_3, takes its place. Whether the 3.25 μ band has actually disappeared is an open question. In mesitylene there is still a trace of the 6.75 μ band of benzene, showing that the benzene "ion" has not been destroyed by the substitution of 3 CH_3 groups. In the xylenes the 6.75 μ band is least effected while the 3.25 μ suffers the most and the whole strengthens the belief mentioned in the beginning that certain vibrating ions always seem to be present but that their effect in absorbing heat waves seems to depend upon their surroundings. Thus the effect of substituting an NH_2 group for an H atom, forming aniline, has the least effect on the benzene, 3.25 μ band, while those from 6 μ to 7 μ have disappeared entirely. In benzaldehyde, C_6H_5CHO, the 3.25 μ band is not seriously influenced by a more intense absorption band at 3.55 μ, while in benzonitrile, C_6H_5CN, and in monobrombenzene, C_6H_5Br, the 6.25 μ band suffers no change.

As a whole, the substitution of a CH_3 or NH_2 group has a great effect on the resulting absorption spectrum. In the benzene derivatives these groups form new bands which occur beside the benzene bands, *showing that the original benzene vibration has not been destroyed.* Such examples as these would indicate that the new bands are due to the groups of atoms substituted. But how are we to establish this with certainty, especially when in the myricyl alcohol the evidence is contradictory for the direct effect of the OH group?

Total Absorption.— This is not so well illustrated here as in the work of Friedel (*loc. cit.*) and of Zsigmondy[1] who used the undispersed radiation. The present work agrees with theirs in showing that compounds having sulphur and the halogens are more transparent than H, O, OH or N which they have replaced. But *not all* the nitrogen compounds are highly opaque, *e. g.*, nitromethane. The present work illustrates best the question of the location of the

[1] Zsigmondy, Ann. d. Phys., 57, p. 639, 1896.

regions of greatest absorption. Thus in pyridine and picoline a layer 0.16 mm. in thickness is almost opaque beyond 6 μ while methyl cyanide is quite transparent. Methyl iodide is quite transparent, since its large absorption bands lie in the region where the radiation from a black body is very weak, while the 3.4 μ band is shallow so that its great transparency, observed by Friedel, as compared with nitrogen compounds is apparently due to the lack of absorption bands in the region of intense radiation [Fig. 10]. As a whole the work agrees with that of Friedel and of Zsigmondy in showing that the absorption of radiant heat depends upon the manner of the bonding of the atoms in the molecule, as well as upon the kind of compound in which the atoms of an element are united.

Friedel and Zsigmondy (*loc. cit.*) found that total absorption does not depend upon the size of the molecule. In the present instance we have noticed that the number and intensity of the absorption bands does not depend upon molecular weight, *e. g.*, in the petroleum distillates. In the present work on dextro-pinene and lævo-pinene the maxima of the bands coincide, showing that the shape of the molecule has no influence on absorption spectra.

Grouping Spectra. — Abney and Festing,[1] say their results indicate "without much doubt that the substances we have examined agree on the whole with that adopted by chemists." In other words certain great groups of compounds have characteristic absorption spectra. This is just what Hartley and Dobbie[2] observed for the alkaloids, in which the ultra-violet absorption spectra vary only in minor details.

These observations apply to the present work. For example, the terpene group of compounds has a series of bands which is common to *all* of the compounds belonging to this group. In the same manner the general trend of their absorption curves is similar. The petroleum distillates have all the principal bands in common, Fig. 11. The spectra of the fatty acids are conspicuous for the lack, but great depth, of their absorption bands, Fig. 7. Having observed that certain groups of spectra are similar, one would naturally search for

[1] Abney and Festing, Phil. Trans., 172, p. 887, 1882.

[2] Hartley and Dobbie, Phil. Trans., 77, p. 846. Also Dobbie and Lawder, Chem. Soc. Jour., 83 and 84, pp. 605 and 626, 1903.

certain characteristic absorption bands; and, reasoning from this standpoint, we may possibly be able to locate the group of atoms which causes the band. Thus, the 2.95 μ band and the OH group of atoms are characteristic of alcohols, while the 4.78 μ band and the NCS radical are characteristic of the mustard oils. But this avails us little for a great many other facts, besides the group of atoms, serve as characteristics of these groups of compounds.

Characteristics of the Spectra of Carbohydrates.—Puccianti (*loc.*

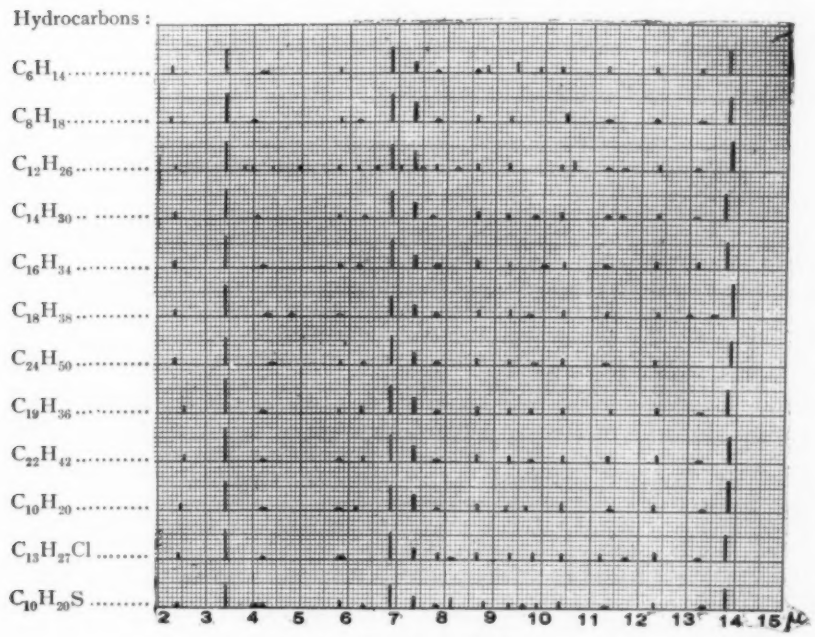

Fig. 11. Petroleum distillates.

cit.) found that in all cases where the carbon atom was joined directly to the hydrogen atom in the molecule, the absorption spectrum showed a band at 1.71 μ. This has been verified in the present work, where the band was found oscillating between the values of 1.68 μ benzene to 1.74 μ for caproic acid, for ethyl succinate, and for methyl acetate. From this point to 3 μ there are numerous small bands of minor importance. Somewhere between 3.1 μ and 3.43 μ a band is found for *every* carbohydrate studied, oscillating from 3.25 μ in benzene to 3.43 μ in the alcohols and compounds rich in

CH_3 groups. In the region extending from 4 μ to 5 μ there is great transparency (except in the case of the mustard oils), and for the more complex compounds, *e. g.*, the petroleum distillates, there are generally no lines even with the large dispersion used. Beyond 5.5 μ the transmission curve decreases, often very abruptly, terminating in strong absorption bands, varying from 6.75 μ in benzene, 6.86 μ in aliphatic compounds [Fig. 10] to 7 μ in terpenes. Beyond this point the bands become stronger, while the transmission curve varies from great transparency to complete opacity. The region at 12 μ is often lacking in absorption bands, and finally we come to a region of frequently great absorption, with bands occurring from 13.6 μ to 14.2 μ. Beyond this point it is difficult to penetrate, but all observations made indicate the existence of similar conditions as in the region investigated.

In addition to the general characteristics of the spectra of carbohydrates it will be noticed, Fig. 6, that the characteristic bands of benzene derivatives are at 3.25 μ, 6.25 μ, and 6.75 μ; that of the aliphatic compounds, *e. g.*, the petroleum distillates, at 3.43 μ, 6.86 μ, and 13.6 μ to 13.8 μ; that of carbon tetrachloride at 13 μ; that of compounds having N or NH_2, at 2.95 μ, and at 6.1 μ to 6.2 μ; that of the fatty acids at 3.45 μ and 5.86 μ; that of the alcohols at 2.95 μ and 3.43 μ; and that of the mustard oils at 4.78 μ, see Table III. The region of great transparency from 4 μ to 5 μ is also to be noticed since the larger dispersion failed to show the presence of strong lines [Fig. 8].

Occurrence of Harmonics. — In discussing the question of the presence of simple relations among the spectral lines in the optical region, Cornu[1] shows that it is useless to search for harmonic overtones since the case is relatively rare. He adds that the law of vibration in whole numbers is applicable only to a particular form of sounding bodies of which the type is a cylindrical column, whose length is great in comparison to the cross-section. In any other type, except this special one, the relations between the vibration numbers of the successive tones is very complex. In Kayser's Spectroscopy, it is remarked that such a search is delusive, and Grünwald's mathematical spectrum analysis[2] is cited as an example

[1] Cornu, Compt. Rend., 100, p. 1181, 1885.

[2] Grünwald, Wien. Ber., 96 to 101, 1887 to 1892.

in which all wave-lengths of the so-called compound spectrum of hydrogen can be converted into corresponding wave-lengths of the water vapor spectrum by multiplying by 0.5. Since then more exact measurements on these lines show that no such relations exist.

Schuster[1] speaks of the iron spectrum which has two lines which are in the ratio of 2 to 3, while hydrogen has lines in the ratios of 20 : 27 : 37. He demonstrates that in accordance with the theory of probability a certain number of coincidences between lines of two spectra might be expected to occur even if the spectra be quite unrelated. Furthermore, there appears to be a tendency for functions formed by two lines to *cluster around harmonic ratios* and "most probably some law hitherto undiscovered exists which in special cases resolves itself into the law of harmonic ratios." Of course, as is well known now, the nearest approximation to such a law is Balmer's Law and the numerous other convergent series formulæ used by Kayser and Runge, and by others. Nevertheless, in spite of these warnings, and fully realizing the danger from lack of dispersion, experimental errors, etc., I venture to call attention to certain marked absorption bands which occur so frequently, in positions which so closely fulfill this relation, that it is necessary to examine more fully into the probable significance.

Abney and Festing (*loc. cit.*) found that compounds having CH_3 groups have a band at 0.74 μ and another between .907 μ and .942 μ, while benzene and CH_3 compounds have a band at .867 μ. Puccianti (*loc. cit.*) found a band at 1.71 for all compounds in which the C atom is joined directly to the H atom in the molecule. Aschkinass (*loc. cit.*) found the absorption bands of water at 1.51 μ, 3.06 μ and 6.1 μ, while Paschen (*loc. cit.*) found them at from 2.916 μ to 3.024 μ, and at 6.06 μ, values which are closely harmonic. Ransohoff (*loc. cit.*) found closely harmonic bands for alcohols at 1.71 μ and 3.43 μ.

In the present work, using a quartz prism, the first band occurs at from .83 μ to .86 μ, while the second one oscillates between the values 1.66 μ for thiophene to 1.73 μ in ethyl succinate. The next disturbance is in the region of 3.4 μ, the maximum being at 3.25 μ

[1] Schuster, Proc. Roy. Soc., 31, p. 337, 1881.

for benzene, and 3.43 μ for compounds rich in CH_2 or CH_3 groups.

The next region where there is a constant recurrence of bands is at 6.75 μ for benzene, and 6.86 μ for other compounds rich in CH_2 or CH_3 groups. In discussing the sources of errors it is shown that the 6.86 μ band is quite accurately known.

Beyond 13.6 μ there is a band of frequent recurrence. In this region, however, it is difficult to locate the bands with great accuracy because of the weakness of the radiation. As a whole, however, the bands at 1.71 μ, 3.43 μ, 6.86 μ and 13.6 μ to 13.8 μ are closely harmonic, *e. g.*, in the petroleum distillates and myricyl alcohol, Figs. 9 and 11, and taken with the .867 μ band of Abney and Festing (.83 to .86 μ in present work) would seem to indicate a vibration about a fixed point (Schuster's clustering). Even if in the future this relation should be found false, the constant recurrence of these bands, in so many compounds, cannot be without meaning. These bands are so sharp and symmetrical that it is difficult to conceive how with greater dispersion they can be resolved into lines which are very unsymmetrically placed about the present centers of gravity.

In carbon tetrachloride, Fig. 10, and tetrachlor-ethylene it was found that this group of compounds is conspicuous for the absence of absorption bands except at 6.5 μ and 13 μ (harmonics) where there are large bands, each of which is evidently complex.

An explanation of the significance of these relations is not attempted and it will be sufficient to add that any such harmonic relation would seem to indicate the resonance of a definite group of atoms, or "ions," to which these lines are solely due. But to attribute a given line to a certain group of chemical atoms is dangerous; for it has already been shown in the case of the mustard oils that the manner of grouping of the atoms is not the only characteristic of this group of compounds. Thus, the physical properites of benzene and thiophene are so similar that these two compounds are readily confounded,[1] yet their absorption spectra are entirely different. It might be added that in the gases, where one would naturally expect such harmonic relations, only acetylene at 3.7 μ and 7.4 μ and methyl ether at 3.45 μ and 6.9 μ have bands satisfying this condition.

[1] Smith's (Richter) Org. Chemie, Vol. 2, p. 47.

Whether this relation will ultimately be proved absolutely true, remains to be seen. To determine this question a very much larger dispersion will have to be employed than has yet been available. This means a far more sensitive recording apparatus than has yet been devised.

In dismissing this question, it will be sufficient to add that after a year's struggle with it, to prove or disprove it, the result has been a closer agreement in the values first obtained, especially for the bands at 3.43 μ and 6.86 μ, Fig. 8. The agreement is as close as one would expect from our present knowledge of the infra-red dispersion of rock-salt. It is quite possible that the 3.43 μ, 6.86 μ and 13.8 μ bands belong to a slowly converging "spectral series," in which case there ought to be a discrepancy in the above harmonic at 13.8 μ.

Absorption of Solids in Solution. — In the ultra-violet Hartley and Dobbie (*loc. cit.*) have studied the absorption spectra of solids dissolved in water. They found that groups of chemically related compounds have similar absorption spectra. In the visible spectrum we also find absorption bands, especially when the solute is a colored substance. Iodine is an example of this type. But in the infra-red the writer found iodine transparent beyond 1.1 μ. As far as is known to the writer, only one other substance, sulphur in CS_2, has been examined far out in the infra-red. This was done by Julius (*loc. cit.*) who found that S had no appreciable effect upon the transparency of the CS_2.

That a solid in solution should be transparent to infra-red radiation seemed doubtful. It would indicate a resonance of small particles, in the optical region, as distinguished from the intra-molecular resonance of the solvent.

After studying so many compounds it seemed imperative to consider this question more thoroughly.

It was suspected that this transparency is simply due to the thin cell used, and to the slight solubility of the solids. For example, assuming that .05 gr. of iodine per c.c. are dissolved in CS_2, using a cell .3 mm. thick, this would be sufficient to form a solid film only .03 mm. It seemed that the proper method of answering this question would be to select a solid having a *strong* absorption band in a region of the spectrum where the solvent has *no absorption bands.*

DIPHENYL, $C_{12}H_{10}$.

The curves of carbon tetrachloride, CCl_4, showed no marked bands up to 6.5 μ. Accordingly this liquid was selected for a solvent. The sample used with diphenyl showed the water band at 2.9 μ and a second band at 4.5 μ. A saturated diphenyl solution showed an additional large band at 3.25 μ which is the characteristic band of the benzene nucleus. This is of considerable interest since diphenyl, $C_6H_5—C_6H_5$, is a double benzene ring. The curve, Fig. 12, shows that solids in a solution do absorb heat waves, and that the selective absorption of a solid in solution and that of the solvent are identical.[1] It also shows that the *benzene vibration still exists*, and that solids in solution can be studied in the infra-red as in the ultra-violet.

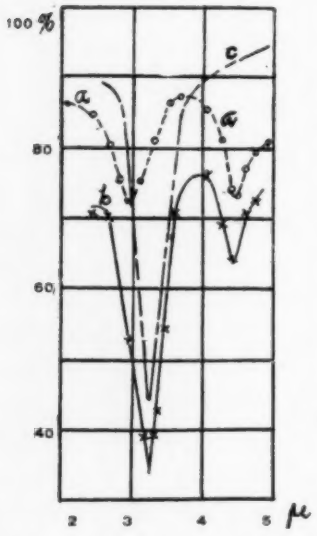

Fig. 12. Curves: a = CCl_4; b = sol. diphenyl, $C_{12}H_{10}$, in CCl_4; c = transmission through $C_{12}H_{10}$.

However, in the infra-red we have no transparent solvents, as is true of the ultra-violet. Water is the most common solvent; but, of all substances examined, it is the most opaque to infra-red radiation. Crystalline solids are not applicable because of their scattering effect, so that many solid compounds of interest on account of their structure cannot be studied because of the lack of a suitable solvent.

NAPHTHALENE, $C_{10}H_8$.

Naphthalene was also examined at 3.25 μ. Its solubility in CCl_4 is unusually great, *e. g.*, the present solution contained .25 gr. per cubic centimeter of CCl_4. This is sufficient to make a homogeneous solid film .28 mm. thick (sp. gr.= 1.15, cell = .6 mm.).

This compound is of considerable importance since its molecule is formed by the condensation of two benzene nuclei. As a result

[1] In my preliminary communication on Infra-red Absorption Spectra, Astrophys. Jour., XX., p. 215, 1904, it appeared to me that there might be a difference.

the cismical properties are quite different from that of benzene; but its absorption spectrum, Fig. 13, shows the 3.25 μ band of benzene, with which it is also comparable in general transmission. As a whole, for the region investigated, this compound shows that the vibration of the benzene nucleus has not been disturbed.

AZOBENZENE, $C_6H_5 - N = N - C_6H_5$.

This compound is also quite soluble in CCl_4 so that a saturated solution contained about .2 gr. per c.c. of the liquid. As with the preceding compounds the rock salt cell was .6 mm. thick.

The curve *d*, Fig. 13, shows the 3.25 μ benzene band, indicating that the presence of the N atoms does not disturb the vibration of the benzene nucleus. This solution is far more opaque than the preceding, showing the effect of the introduction of the N atoms, just as in other compounds containing nitrogen.

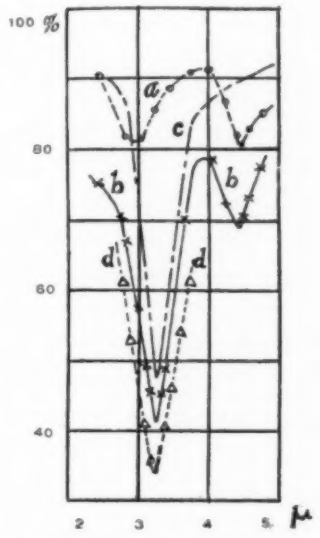

Fig. 13. Curves: a = CCl_4; b = Napthalene, $C_{10}H_8$, in CCl_4; c = transmission through $C_{10}H_8$; d = Azobenzene in CCl_4.

Moreover, this solution is of a reddish-brown color, showing an absorption band in the visible spectrum, as well as in the infra-red. This shows that both are due to an intramolecular disturbance and disapproves the idea of a resonance of small particles (of molar dimensions, as for example, Kosonogoff's butterfly scales and Wood's metal films) in the optical region, as distinguished from the intramolecular resonance in the infra-red. Of course, one might say that the infra-red band, *e. g.*, the 3.25 μ band, is also a resonance effect. Possibly it is but the evidence of a resonance of small electrically charged particles, whose capacity and hence whose periods (like a condenser) depend upon their proximity to similarly charged particles (the closer the particles, the greater the capacity, hence, the slower the period and, hence, the farther is the

absorption band shifted toward the longer wave-lengths) is somewhat contradictory in the infra-red.

SUMMARY.

The infra-red absorption spectra of organic compounds have been studied, the majority to 15 μ, using a radiometer, two mirror spectrometers and rock salt prism. Out of a total number of at least 135 compounds examined with the rock salt prism, 131 have been recorded in this paper. They include solids, liquids, and gases. In addition to this, 19 compounds were examined to 2.7 μ, using a quartz prism.

The following are some of the results obtained:

1. A study of isomeric compounds shows that the arrangement or bonding of the atoms in the molecule, *i. e.*, its structure, has a great influence upon the resulting absorption spectrum, which agrees with Julius.

This is of considerable significance, and is in marked contrast with stereomeric compounds, like dextro- and lævo-pinine, which were found to have identical spectra, showing that the spacial arrangement of the atoms, *i. e.*, the configuration of the molecule, had no effect upon the resulting absorption spectrum.

2. No shifting of the maxima with increase in molecular weight, "Kundt's Law," could be detected, except in the case of the band lying between 3.1 μ and 3.5 μ, for gases. Instead of a shifting of the band in certain compounds there occurs a new band beside the original one when a methyl- or amido-group is substituted for a hydrogen atom, the new band lying toward the longer wave-lengths when a methyl-group is substituted, and toward the shorter wave-lengths when the hydrogen atom is replaced by an amido-group. This disagrees with investigations of Krüss in the optical region, where *only the new band* was observed.

3. A rise in temperature of 20° had no effect upon the transparency of the compound, nor upon the position of its maxima.

The effect of replacing an H atom by certain groups of atoms like NH_2 and CH_3 is very marked, and usually shows new bands, *e. g.*, 2.96 μ and 3.43 μ, in the resulting absorption spectrum. In the spectra of certain benzene derivatives, however, the bands of the

benzene spectrum are usually present, showing that the vibration of the benzene nucleus has not been destroyed. However, the writer does not consider this sufficient evidence to consider the new bands to be due to the groups of chemical atoms substituted.

5. Total absorption is not influenced by the size of the molecule; while compounds having sulphur or halogens are more transparent than those having H, O, OH or N which they have replaced, just as found by Friedal and by Zsigomondy.

6. The spectra of groups of compounds are similar and are characteristic of the grouping adopted by chemists, as found by Abney and Festing, for the region of 1 μ.

7. Carbohydrates have a characteristic spectrum, with absorption bands at .83 μ to .86 μ, 1.67 μ to 1.72 μ, 3.25 μ to 3.43 μ, 6.75 μ to 6.86 μ, and 13.6 μ to 14 μ. The first large absorption band in carbohydrates occurs in the region of 3.2 μ, which is in general followed by a *transparent* region from 4 μ to 5 μ. The work of Puccianti, in which he found that all carbohydrates have an absorption band at 1.71 μ while benzene derivatives have two additional bands, at 2.18 μ and 2.49 μ respectively, has been confirmed on 18 new compounds. The 1.7 μ band deserves especial notice.

8. In addition to the characteristic carbohydrate spectrum, certain bands in it occur in positions which are close harmonics, the maximum wave-length of each succeeding band being twice the preceding. The question whether this is merely a coincidence or whether it is an exact relation is not fully determined. To decide this question a larger dispersion will be necessary, while the spectrum will have to be explored to 27.6 μ for the next harmonic. In the same manner more pairs of bands will have to be located in the ammonia spectrum in order to show that the constant difference of the wave numbers found is not merely a coincidence, hence, that there is a true spectral series present.

8. The three isomeric xylenes have banded, "channeled," spectra in which the most important line, in each group, lies farthest toward the long wave-lengths, in the order: *ortho*, *meta*, *para*. In other words the *ortho*, in which the CH_3 groups are the closest together in the benzene ring, has the "head" of each group of bands lying farther toward the infra-red than are the heads of the corresponding bands of the meta- and para-compounds.

10. In many compounds numerous bands are in coincidence, which would no doubt be found in different positions, when using a larger dispersion. Other bands, like the one at 3.25 μ in benzene, in benzaldehyde, and in pyridine, or the 3.43 μ and 6.86 μ bands found in aliphatic compounds, seem to point to a specific group of atoms or to some "ion" or "nucleus" common to them, as their source.

The most marked example of this type is phenyl mustard oil in which the vibration characteristic of the mustard oils, at 4.78 μ is *superposed* upon the vibration of the benzene "nucleus" or "ion" which has its maxima at 3.25 μ, 6.75 μ etc. In some compounds there is evidence that certain bands, *e. g.*, the 3.43 μ band, are due to a definite group of atoms, *e. g.*, the CH_3 groups in the chain compounds and terpenes; in other compounds the evidence is just as strongly in favor of the manner of bonding of the atoms, *e. g.*, the methylene hydrocarbons of the petroleum distillates; other compounds, *e. g.*, benzene and its derivatives, especially phenyl mustard oil, in which we have the characteristic vibration of the mustard oils superposed upon the vibration of the benzene nucleus, show that both the groups of atoms and their manner of bonding with other atoms, as well as the kind of atom, have a great influence upon the absorption curve.

TABLE III.

Compounds Having the Following Groups:	Show Characteristic Absorption Bands at:		
CH_2 or CH_3	3.43	6.86	13.6–13.8 and 14 μ
NH_2	2.96	6.1 to 6.15 μ	
C_6H_6	3.25 μ	6.75 8.68 9.8 11.8 12.95	
NO_2		7.47? 9.08	
OH	2.95		
NCS		4.78	

In the present work the spectra have been discussed from the standpoint that, since compounds of the same chemical composition (isomers) have different spectra, the source of the disturbance is intramolecular. If we had assumed ignorance of the composition of the compounds, we would have expected, from our knowledge of the spectra of the elements, that each compound ought to have

a different spectrum. This has been found to hold true, except for certain lines in them. There would be no reason for deciding whether the cause is inter- or intra-molecular. The compounds might then be grouped according to the marked absorption bands which they have in common, *e. g.*, those having a band in common at 3.25 μ, at 3.43 μ or at 4.78 μ. One compound (phenyl mustard oil) would then be placed in the 3.25 μ and in the 4.78 μ group. Another (xylidine) would belong to the 2.95 μ group and to the 3.43 μ group. This would then suggest a disturbance common to both groups, and we are brought to the point arrived at, by the other line of argument ; viz., there is a something, call it " particle," " group of atoms," " ion," or " nucleus," in common with many of the compounds studied, which causes absorption bands, characteristic of the great groups of organic compounds, but we do not know what that " something " is.

The presence of these groups of " ions," each group having its own free period of vibration, is in accord with the present conceptions of absorption and anomalous dispersion. To assign the cause of the absorption bands, given in Table III., to a particular group of chemical atoms rather than to a less definite, ultra-atomic, source, does not elucidate matters very much, although it is true that these bands do *not* appear until these groups of atoms are introduced into the compound.

This investigation has placed the writer under obligations to numerous persons, to all of whom he is very grateful for services rendered. In particular would he mention Professor E. L. Nichols and E. Merritt, of the Dept. of Physics ; Professors L. M. Dennis, W. R. Orndorff and Dr. J. R. Teeple, of the Dept. of Chemistry ; Professor A. C. Gill and H. Reis, of the Dept. of Geology, and Professor C. F. Mabery, Case School of Applied Science, who through advice or the loan of materials have furthered the work.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY,
January, 1905.

THE ELECTRIC ARC IN A VACUUM.

BY C. D. CHILD.

THE following is an account of experiments on the electric arc in a vacuum and in hydrogen, using different substances as electrodes. It is a continuation of work previously described in the PHYSICAL REVIEW,[1] where a description of the apparatus may be found. As before, a mercury pump was used for exhausting the tube. A standard Weston voltmeter and a Whitney ammeter were used for measurements. A McLeod gauge was attached to the pump for measuring pressures less than 1 mm.

Arc Between Graphite Terminals. — The first observations were made on the arc between graphite terminals. They were purchased of the Acheson International Graphite Company, and consisted of rods 12.5 mm. in diameter. The current was derived from a 110-volt dynamo, resistance being put in series with the arc. At atmospheric pressures the arc was quite irregular, but the average drop in potential at the anode and at the cathode appeared to be much the same as with carbon. The electric force through the arc, however, was much greater.

At lower pressures it was possible to make measurements, and these are given in Table I. Column 1 gives the pressure of the gas in millimeters of mercury; column 2, the drop on the anode; column 3, that at the cathode; column 4, the total potential difference about the arc. The length of the arc was approximately 2 mm. The potential within the arc was determined by inserting in it a carbon pencil, or a platinum wire. For pressures greater than 1 mm. a carbon pencil was used; for less pressures the platinum wire. The exploring pencil was in each case placed as nearly as possible in the center of the arc.

The most noteworthy fact here shown is the peculiar change which takes place when the pressure is lowered below 1 mm. The

[1] PHYS. REV., 19, 117.

TABLE I.

Pressure of Gas.	Drop in Potential at Anode.	Drop in Potential at Cathode.	Potential Difference Between Electrodes.
200	25	15	40
80	22	16	38
30	21	15	36
10	20	14	34
1	15	14	30
.8	7	13	20
.3	6	13.5	20
.02	5	13	18

drop at the anode becomes much smaller, so that it is less than that at the cathode.

This, however, is not a constant condition. Even with the lowest pressure there would often be a sudden jump in the potential difference at the anode and a decrease in that at the cathode. This tendency was more noticeable at pressures of .7 or .8 mm.

At pressures in the neighborhood of 1 mm. there are usually striations but with the lowest pressures none were observed. There was a bright spot on the cathode from which particles were driven off in straight lines so that it appeared as if the current was proceeding from that point.

Occasionally there would appear a glow on some part of the anode, and whenever this appeared the drop in potential there rose from 5 volts to 15 or 20. In other words the glow at the anode and the large drop in potential are parts of the same phenomenon. Very much the same phenomenon was observed by Mills[1] when working with the mercury arc.

It was found that the pressure at which the glow appeared depended to a slight extent upon the length of the arc. With a pressure of .7 mm. the electrodes must be as near as 2 mm. in order to cause the glow to disappear; at .35 mm. the length could be 5 mm.; and at .1 mm. it could be 14 mm., or even more. It appeared to make no difference which electrode was above.

At a pressure of .4 mm. the current was varied from 6 to 25 amperes without producing any apparent effect on the potential difference.

[1] PHYSICAL REVIEW, 19, 69.

As has been stated the current appeared to emanate from the bright spot on the cathode. It was, therefore, thought that if a piece of platinum was placed in the arc, some effect might be observed such as appears when an obstacle was placed in the path of cathode rays. A piece of platinum foil 2 mm. square was accordingly placed in the arc, the plane of the foil being perpendicular to the length of the arc. No shadows were cast, but it was found that when the platinum was in the arc the glow at the anode was much more apt to appear and the potential difference about the arc to be correspondingly increased.

This was still more noticeable when the size of the foil was increased. Thus a piece of foil 8 mm. square was placed in the arc, when the pressure was .4 mm. Without the foil no glow appeared at the anode, but when it was inserted the glow always appeared. It apparently made little difference whether it was placed near to the anode, or to the cathode. The bright spot on the cathode appeared, in general, to move away from the foil, but often it did not do so, and at such times the foil would become red hot immediately in front of the bright spot.

A hole 1.5 mm. in diameter was made in this larger piece of platinum. The glow still appeared and the space between the anode and the opening was generally brighter than the remaining space. When the foil was near to the anode the glow would appear to extend through the opening toward the cathode, as if it was caused by ions driven off from the anode.

The conductivity of the arc in the region near the anode was tested both with and without the glow. This was done by placing two platinum wires in the arc and connecting them to an E.M.F. of four volts and a galvanometer of seventy ohms resistance. The air was pumped out until the pressure was less than .4 mm., so that normally no glow appeared. It could then be produced when desired by inserting the platinum foil in the arc. The current between the platinum wires varied continually from .01 to .001 ampere, but in general it appeared to be less when the glow occurred at the anode, showing the conductivity was greater when there was no glow.

The Arc in a Magnetic Field. — When a magnetic field was produced about the arc at a pressure of .7 mm. or less, the gas in all

parts of the tube became more luminous than before, and a bright stream appeared to run from the arc along the lines of force toward the magnet. When an electro-magnet bent in the form of a nearly completed circle was placed about the arc, the luminous streams extended in both directions from the arc toward the ends of the magnet, and the part of the tube where the field was strongest was brighter than the remaining part. The luminous glow along the lines of force can probably be explained by the tendency of ions to follow magnetic lines of force.[1]

There were other phenomena for which I know no explanation. For example when the magnetic field was produced there was a glow through the gas on the side toward which a wire would have been displaced, as if it was carrying a current in the same direction as that flowing through the arc. At the same time there was a glow about the anode on the opposite side from this. It is conceivable that the glow about the cathode was caused by positive ions which were deflected by the magnetic field, but it would not seem possible that that about the anode was caused by negative ions, since both the positive and negative ions would be deflected in the opposite direction from this glow.

Moreover, if the platinum foil was placed so that the glow extended from the anode upward through the opening in the foil, and if the magnetic field was then produced about the arc, the glow above the foil became less distinct and at the same time moved in the same direction as that about the anode.

It has been observed by Skinner[2] that the fall of potential at the anode with discharge in a vacuum depends on the kind of metal used as the anode. Aluminum was accordingly substituted for the graphite anode, but the fall of potential appeared to be the same as before. This, however, proved nothing since the aluminum became coated with a layer of carbon before any measurements could be taken.

At pressures of about 1 mm. a very slight glow appeared on the cathode and also on any obstacles in the neighborhood of the cathode. It appeared as if blown by draughts of air coming from

[1] Thomson's Conductivity of Electricity through Gases, p. 791.

[2] Wied. Ann., 68, 752.

the bright spot on the cathode, reminding one very much of drifting snow.

The tube became coated after a time with carbon, so that it was impossible to see the gaseous part of the arc.

When the graphite was first heated in a vacuum it gave out some gas, but after it had been heated and then the air pumped out several times, the vacuum improved on producing the arc. Thus at one time the pressure decreased from .4 mm. to less than .01 mm. without any air being pumped out. Whether this was due to some chemical action taking place or to some other cause is not known.

Arc between Carbons in a Vacuum. — The arc between carbons has already been investigated, but after observing the phenomena with graphite it seemed well to secure lower pressures than those previously used. It is more difficult to do this with carbon than with graphite but one as low as .1 mm. was secured. At this pressure the potential difference about the arc was continually varying, so that it was impossible to make accurate measurements. The voltage would gradually increase from 20 to 30 or 35 volts and would then suddenly decrease to less than 20. With this gradual increase in voltage the gas in the tube became more and more luminous, becoming suddenly less luminous when the voltage dropped to the lower value. This tendency to fluctuate became more noticeable as the pressure of the gas was diminished.

With the fluctuation of the total voltage about the arc there were corresponding changes in the drop at the anode and at the cathode. In each case the drop increased as the tube became more luminous. This drop was measured by inserting a platinum wire in the arc. As nearly as one could judge the average drop at the anode was 8 volts, that at the cathode 10 volts and the total drop was 18 volts.

Arc between Copper Terminals. — The next experiments were performed with copper. The copper terminals were rods 12 mm. in diameter and 5 cm. long. There are given in Table II. the data for pressures varying from 30 mm. to 2 mm. Column 1 gives the pressures; column 2, the drop at the anode; column 3, that at the cathode; and column 4, the total potential difference about the arc. The conditions were the same in this experiment as with graphite.

With lower pressures the arc could not be maintained.

TABLE II.

Pressure of Gas.	Drop in Potential at Anode.	Drop in Potential at Cathode.	Potential Difference between Electrodes.
30	20	12	32
10	20	11	31
4	18	11	29
2	10	10	20

Arc between Iron Terminals. — With iron in a vacuum the phenomena were much the same as with copper. The fluctuation in the drop at the anode began at a higher pressure than with copper. On the cathode were many bright spots instead of one as with graphite, and there was a continual rose-like glow at the anode. There were no striations when using a 110-volt circuit.

When using a 300-volt circuit, the total drop about the arc was as much as 150 volts at a pressure of 2 mm., and there were many striations. It was not often possible to maintain the arc between either iron or copper at these low pressures long enough to heat them to a red heat. A deposit was quickly formed on the tube with the metals, so that after the arc had been running a few seconds, it was impossible to see what was happening in the gaseous part of the arc. After removing the metals any oxide on their surface was found to be reduced, the copper having the usual color of clean copper and the iron being white, appearing much like tin.

A little air was let into the tube and it was again exhausted, and it was found to be more difficult to maintain the arc at a pressure of about 2 mm. than before.

It has already been pointed out by Stark that an oxide on the metal causes an arc to pass with greater ease.[1] This, no doubt, is the cause of some of these phenomena. When the air is first pumped out the arc can be maintained without great difficulty, but after the oxide on the surface of the metal is reduced this can not be done, so that measurements on the arc between metals in a vacuum are of little value, so long as the surface of the metal and the constitution of the surrounding gas are varying. The behavior of the arc with the metals and with graphite are thus seen to be radically different.

[1] Physik. Zeit., 5, 81.

Arc between Graphite and Various Metals. — A series of experiments was also tried using graphite as one of the terminals and for the other one of the following metals — platinum, iron, nickel, copper, silver, aluminum, antimony, zinc, lead, cadmium, bismuth and tin.

It was found that in all of these cases when the graphite was negative the behavior of the arc was much the same as when both terminals were graphite. In other words, with a pressure of less than 1 mm. the character of the anode has little or no effect on the arc. On the other hand at this pressure the character of the cathode had a very great effect on the arc. When the graphite was positive it was very difficult to secure an arc with some of these metals and very easy with others. Thus on a 100-volt circuit it was impossible to maintain an arc with platinum, iron, silver, copper or nickel, and very easy with the other metals in the above list.

The first experiments were with iron for one of the electrodes, using the same piece of iron that had been used in the preceding experiments, and as stated it was not possible to maintain an arc with this as cathode. The same statement may be made concerning copper.

An arc was then produced between graphite and platinum. It was more difficult to secure a vacuum in this case, since the platinum on heating gave off much gas. The platinum was 1 mm. in diameter. It was also impossible to use large currents, since the platinum was then melted, but the phenomena were practically the same as with iron. A platinum bead weighing 1.3 g. was placed in a depression that had been drilled in an iron rod. This was used as the lower terminal with the same result as before. If, however, the platinum was brought to red heat by being made the anode, it could then be used as the cathode and the arc maintained for several seconds. As long as the arc was thus maintained there were many bright points on the platinum. The platinum was apparently vaporized and sparks were driven off from it, so that it lost much in weight.

Other metals were then used and since some of these melted very easily, they were placed in the depression in the iron rod. Since no arc can be formed in a vacuum when using iron as the

cathode, it seemed safe to use this to hold the various metals, and it was found that whenever the arc could be maintained in a vacuum, the negative end always rested on the metal in the cup, and not on the iron. After using any metal all parts of the tube were carefully cleaned, before using a different one.

In this way it was found that an arc could not be maintained on a 100-volt circuit with a pressure of less than 1 mm. when using nickel or silver for the cathode. When using aluminum as cathode it was possible to maintain an arc, if the aluminum was first heated by being made the anode for a brief time. Otherwise it could not be so used. Metals having a lower melting point could be used as the cathode.

In Table III. the data are given concerning the metals. Column 1 gives the name of the metal; column 2, the drop in potential at the metal when used as the cathode. When no number is given in this column it signifies that no arc could be maintained when using the metal as the cathode. Column 3 gives the melting point of the metal as given in Everett's C.G.S. System of Units. The current used was 10 amperes, the E.M.F. of the circuit was 100 volts, and the distance between the electrodes 2 mm.

TABLE III.

Metal.	Drop in Potential at Cathode.	Melting Point.	Metal.	Drop in Potential at Cathode.	Melting Point.
Platinum		1775°	Antimony....	8	432°
Iron		1600	Zinc	9	412
Nickel		1450	Lead.....	8	326
Copper.....		1054	Cadmium.....	7	315
Silver.		954	Bismuth.....	6	260
Aluminum	19	600	Tin.....	8	230

In all of these cases the total fall in potential about the arc was approximately six volts more than that at the cathode.

To this list may be added sodium, potassium and mercury. Weintraub[1] gives the sum of the drops in potential at the cathode and anode for these to be 8, 8 and 7.5 respectively, while their melting points are — + 96, + 62 and — 40. In general the higher the melting point the greater the drop in potential at the cathode necessary

[1] Phil. Mag. (6), 7, 114.

to maintain an arc. The principal exception to this rule was in the case of tin, but the thermal conductivity of the tin is greater than that of the other metals, and it is quite probable that on this account it requires a greater development of energy to keep it in a melted condition. If this is correct, the drop in potential at the cathode is a function both of the melting point and of the thermal conductivity of the metal.

Measurements of the total fall of potential with these metals were made as the pressure of the gas was increased by drawing air into the tube. It was found that with higher pressures all of these metals could be used as the cathode. It was also found that in all cases the fall in potential about the arc was increased as the pressure of the gas was increased. The series of readings for these potential differences when lead was used as the cathode is given in Table IV. The readings taken with the other metals were quite similar to this one.

Table IV.

Pressure of Gas.	Potential Difference About Arc.	Pressure of Gas.	Potential Difference About Arc.
.4	14	200	22
2	15	400	30
6	16	550	30
20	17	730	32
60	19		

At the higher pressures the potential differences fluctuated very much so that the last three readings were of little value.

There was no sudden change in the potential difference found here as there had been with graphite at .8 mm. At pressures of about 1 mm. there was a glow seen at the anode similar to that with graphite, and some fluctuation of the drop at the anode, but this was not at all as great as with graphite.

Arc between Graphite Terminals is Hydrogen.— There is given in Table V. a series of readings with graphite terminals in hydrogen. The conditions are the same as with the other experiments and the readings are arranged as in the first table.

It was difficult to take these readings because there is a large amount of heat developed in the arc in hydrogen, so that the tube was very liable to break. As a result they were often taken hurriedly

TABLE V.

Pressure of Gas.	Drop in Potential at Anode.	Drop in Potential at Cathode.	Potential Difference Between Electrodes.
700	57	65	130
550	45	60	100
400	45	40	85
250	40	40	80
150	40	35	75
100	45	30	75
50	45	30	75
20	40	25	65
6	32	22	54

before the arc had become quiescent. Several sets of observations, however, were taken and there was no question but that the drop at the cathode was greater than that at the anode with a pressure of 700 mm. and that it became smaller than that at the anode at lower pressures. At pressures lower than those given in the table the measurements were the same as with corresponding pressures of air.

At a pressure of approximately 10 mm. there were three different forms of the arc. If 500 volts were applied when the terminals were cooled below red heat, but were still warm, a faint glow would appear about both electrodes even when they had not been brought into contact. The gas between the electrodes would not be luminous and the current was less than 1 ampere and the voltage high.

If the terminals were still red hot when the voltage was applied, a second form of the arc was apt to appear. This consisted of brilliant striations. The voltage here was smaller and the current larger. Finally when the terminals were placed in contact an arc was formed which appeared the same as an arc formed in the air. This last is the form which was used in taking the data given in Table V. These same forms appear again when making the observations on the arc with carbon terminals in hydrogen.

The first two forms of the arc were quite unstable and were liable to break down into the third form. Apparently they required comparatively low temperature of the electrodes and of the gas. It is noticeable that the arc with striations appeared at higher pressures when using hydrogen than when using air. At a pressure of 10 mm. the voltage was independent of the current.

Cored Carbons in Hydrogen. — There are given in Table VI. the data with the arc between cored carbons in hydrogen.

TABLE VI.

Pressure of Gas.	Drop in Potential at Anode.	Drop in Potential at Cathode.	Potential Difference Between Electrodes.
700	85	15	105
400	80	15	95
150	55	30	85
100	45	30	75
15	35	20	55

As has been stated three different forms of the arc were observed when using graphite terminals in small pressures of hydrogen. With cored carbon there was besides these a fourth form. If the pressure was approximately 20 mm. and 500 volts were switched on to the terminals while they were still hot, an arc could be formed without bringing the terminals into contact. At times this would have a peculiar ball-shaped form with striations in spherical layers. The voltage with this was usually greater than 150 volts and at times more than 300 volts. This was very apt to go into the second form described above with transverse striations and having a current of 2 or 3 amperes. At pressures of 15 mm. the arc would form without contact even when the electrodes were no longer hot.

Arc Between Iron Terminals in Hydrogen. — The arc was then tried between iron terminals in hydrogen, but there was very great irregularity. With a pressure of 700 mm. one reading was taken giving the drop at the anode as 50 volts and that at the cathode as 70 and the total as 140. This was with a current of 10 amperes and a length of 4 mm. but it was evident that inserting the carbon in the arc changed its character to a large degree.

At lower pressures the total potential difference was somewhat smaller but the ends of the arc were continually moving from one place to another on the electrode, and the reading of the voltmeter continually showed large variations. It was evident that no measurements would be of value until all oxide was removed from the electrodes, and it is necessary to postpone this work for the present.

Arc with Alternating Currents. — An attempt was made to form an arc with an alternating E.M.F. of 220 volts between iron and

copper and graphite terminals, but with none of these substances was it possible to do so at any pressure, nor could an arc be formed when using graphite as one terminal and iron for the other. The result with the metals was to have been expected, but it seemed surprising that no alternating current could be obtained with graphite, since this in many ways behaves like carbon.

Theoretical Considerations. — There are three points of theoretical interest in these experiments. First they show that the phenomena of the arc depend very largely on the character of the electrodes and of the gas in which the arc is formed. It is indeed already known that the arc is more or less influenced by such conditions, but that it could be so largely changed had not before been shown. It would thus appear probable that there are chemical reactions taking place in the arc and that its behavior depends very largely on these reactions. This also had been indicated by the work of Stark[1] on the effect of the oxide at the cathode, and by that of Mrs. Ayrton[2] on the hissing arc. But the importance of considering the chemical reactions has been emphasized by these experiments.

If this be so, then no explanation of the arc which fails to consider the chemical reactions can be considered complete. Thus for example it has been suggested that the greater part of the current is carried by negative ions and that these are produced by the high temperature of the cathode. We find, however, that in a vacuum it is easy to maintain an arc with such substances as mercury and cadmium for the cathode, while it is impossible to maintain one with platinum, iron, or nickel for the cathode, and yet these latter substances can be raised to higher temperatures than any in the first group. In fact all of the data for the assumption that the negative ions in the arc are produced by the high temperature of the cathode are drawn from experiments on platinum in a vacuum, and yet this is one of the substances which cannot be used for the cathode of the arc in a vacuum. Apparently some other explanation than this is necessary to explain the negative end of the arc.

A second point of interest is the relation shown between the melting point of a metal and its use as cathode. This point also is

[1] Phys. Zeit., 5, 81.

[2] The Electric Arc, 298.

not entirely new. It has been suggested that to have an arc it is necessary to have either chemical or physical change at the terminals. In the light of our present knowledge it is evident that it is not necessary to have any change at the anode, and the experiments of Weedon[1] indicate that it is not even necessary that any change should occur at the cathode, for he found that with water-cooled copper terminals in hydrogen the amount of copper consumed was not more than 4 mg. for a current of .35 amperes running for 1.5 hours. However, this form of the arc is very different from the common form and the cause of the ionization may be quite different in the two forms.

Though we are not in a position to say whether chemical or physical changes are essential, we can say that they both aid in the production of the arc. We can easily see how chemical action can do this, since we know that such action is very generally accompanied by ionization, but it is not known that ions are produced by fusing or boiling. It is, however, altogether possible that ions are more easily formed by impact or by any other means at the moment when physical change is taking place.

An alternative explanation is that ions are not produced in the metal itself, but in the layer close to the metal and that this layer may be kept at a high temperature more easily when ebullition is occurring. This may possibly be similar to the separation between a hot metal and a liquid, in the spheroidal state. Further experiments will be necessary to decide whether either of these, or whether some third explanation is correct.

The third point of interest is the change which takes place at the anode with graphite terminals and with a low pressure of the gas. When the pressure is less than .7 mm., the arc appears to possess a form intermediate between the ordinary arc and the ordinary vacuum discharge. The arc here has a small drop in potential at the cathode similar to the ordinary arc, and also a small drop at the anode which is similar to the vacuum discharge.

A possible explanation is that with the ordinary vacuum discharge and with the arc at sufficiently low pressure whatever positive ions there are going from the anode, leave it with too small a velocity

[1] Paper presented at the meeting of the American Electrochemical Society, April, 1904.

to produce any ionization by the impact. As the pressure decreases the velocity of the ions per unit electric force, must decrease, and consequently the number of ions becomes inadequate to carry the current. There would then be caused a large potential difference at the point where there was the most difficulty in carrying the current. This point is apparently at the anode. With this increase in the potential difference the velocity of the positive ions would soon be large enough to produce ionization by their impact. If this explanation is correct, the glow at the anode must be essentially the same as that caused by the "Canalstrahlen."

This explanation does not indeed account for the suddenness of the change at the anode, when both electrodes are graphite. This, however, is apparently not the normal condition, since the change is never so sudden with other substances.

Summary. — Experiments were performed between different kinds of electrodes in a vacuum and in hydrogen. With graphite terminals, it was found that with pressures less than .7 mm. the drop in potential at the anode became less than that at the anode, and that whenever a glow appeared at the anode the drop there increased from 6 volts to 15. There are reasons for believing that this glow is similar to that seen with "Canalstrahlen."

At pressures of less than .7 mm. many of the ions appear to move along magnetic lines of force when in a magnetic field.

With carbon terminals and with a pressure of .1 mm. the drop at the cathode was somewhat larger than that at the anode.

With copper and iron it was found impossible to maintain an arc with pressures of less than about 1 mm., unless there was an oxide of the metal on the cathode. Experiments were performed using graphite for one of the terminals and various metals for the other. When the cathode was graphite the phenomena of the arc were practically independent of the nature of the anode. It was, however, impossible to maintain an arc on a 100-volt circuit with a pressure of less than 1 mm. when the anode was graphite and the cathode any of the metals having a high melting point, such as platinum, iron, nickel, copper or silver. It was very easy to do so when the metal was one having a low melting point such as antimony, lead or bismuth.

With graphite terminals in hydrogen the drop at the anode was less than that at the cathode for pressures above 400 mm., the total drop being much greater than with the arc in air. Between 400 mm. and .7 mm. that at the anode was the greater. At pressures less than 10 mm. the arc would start on a 500-volt circuit without bringing the terminals in contact, if they were comparatively warm. Under these conditions there were three distinct forms of the arc.

With carbon in hydrogen the drop at the anode was much greater than that at the cathode. With low pressures four forms of the arc were here observed.

No current could be produced by an alternating E.M.F. of 220 volts between iron, copper or graphite terminals at any pressures.

From the experiments it would appear that no theory of the arc is complete which fails to consider the chemical action occurring in the arc. It would also appear that the temperature of the cathode does not alone account for the production of ions there, and their production depends very largely on the melting point of the metal used.

The experiments also indicate that with pressures less than about .8 mm. the positive ions driven off from the anode ionize by impact the gas about the anode, while with less pressures this does not occur.

Aid was received from the Carnegie Institution in purchasing the apparatus used in the work and the greater part of the work was performed at the Physical Laboratory of Cornell University. I desire, therefore, to express my appreciation for this kindness both to the Institution for the grant and to Professor Nichols for permission to work at the Cornell Laboratory, and to Professor Shearer, of Cornell University, for the assistance he gave me while doing the work.

COLGATE UNIVERSITY,
February, 1905.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-EIGHTH MEETING.

A REGULAR meeting of the Physical Society was held in the Ryerson Physical Laboratory of the University of Chicago, on Friday, April 21, and Saturday, April 22, 1905. President Barus presided.

In the absence of the Treasurer the Treasurer's Report for the year 1904 was read by the Secretary and on motion accepted.[1]

The following papers were presented:

1. On the relation between the Radioactivity and Composition of Uranium Compounds. H. N. McCoy.

2. The Residual e.m.f. of the Carbon Arc. G. G. Becknell.

3. The Radius of Molecular Attraction. C. W. Chamberlain.

4. The Relation between Potential Difference and Spark Length for small values of the latter. G. M. Hobbs.

5. Short Spark Discharges. Carl Kinsley.

6. The Influence of Electrodes upon Spark Potentials. J. E. Almy.

7. Note on the Potential Difference required to produce very short sparks. J. E. Almy.

8. Some Oddities in Lenses. A. B. Porter.

9. On the Variation of a Capacity with Temperature. E. M. Terry.

10. On the possible variation of Inductance Standards with Temperature. A. H. Taylor.

11. On the Comparison of Mutual Inductances. A. H. Taylor.

12. The Comparison of the Mutual Inductance of a pair of coils with the Self-induction of one of them. R. T. Herdegen.

13. The use of the Quadrant Electrometer in Measuring Current. O. M. Stewart.

14. Polarization of Standard Cells. R. R. Ramsey.

15. Variation of Arc Spectra with the Phase of the Current producing them. Henry Crew and B. T. Spence.

16. Reciprocal Relations in Diffraction. A. A. Michelson.

17. Report of Progress in Ruling Diffraction Gratings. A. A. Michelson.

[1] The report is printed on p. 380.

18. On the Use of the Concave Mirror with Diffraction Gratings. A. A. Michelson.

19. The Relative Positions of the Arc and Spark Lines in the Spectra of Titanium and Zinc. N. A. Kent.

20. The Resolving Power of Quartz Prisms. H. M. Reese.

21. The Black Spot in Their Liquid Films. E. S. Johonnott.

22. Thermal Conductivities. F. L. Bishop.

23. The Collapse of Tubes by External Pressure. A. P. Carmen.

24. Abbe's Diffraction Theory of Microscopic Vision. A. B. Porter.

25. Surface Tension by the Method of Liquid Jets. F. R. Watson.

26. Diffraction Fringes of Electric Discharges and of Fluid Streams. A. L. Foley and J. H. Haseman.

27. On Dielectric Strain Along the Lines of Force. L. T. More.

28. On the Dielectric Strength of Crystals. J. E. Almy.

29. The Velocity of Ions in Gases from Colored Flames. (By Title.) Percival Lewis.

30. The Kerr Effect in the Infra-Red Spectrum. L. R. Ingersoll.

31. The Phosphorescence of Sidot Blend. E. L. Nichols and Ernest Merritt.

32. Infra-Red Emission Spectra of Gases in Vacuum Tubes. (By Title.) W. W. Coblentz.

33. Æther Drift and the Rotary Polarization Test. D. B. Brace.

34. On a test of Anomalous Dispersion by means of Channeled Spectra. D. B. Brace.

35. The Absorption and Refraction of Carbon. H. A. Clarke.

36. Experiments on the Flow of Electricity in Metals under Changes of Pressure. C. B. Thwing.

37. Note on Fleeting and Persistent Nuclei in energized, dust free Air. (By Title.) Carl Barus.

Adjourned.

ERNEST MERRITT, *Secretary.*

TREASURER'S REPORT, January 1, 1905.

RECEIPTS.

Balance brought forward	$1,557.11	
Interest on balance	54.50	
Arrears of dues paid during 1904	37.50	
Life membership fees; two	100.00	
Annual dues for 1904; 232½	1,162.50	
Total		$2,911.61

DISBURSEMENTS.

Subscriptions to the Physical Review, 245½	$ 736.50
Subscriptions to Science Abstracts, 231	346.50
Andrus and Church for printing and supplies	71.31

Drafts and collections on checks	3.05	
Expenses of Committee on Notation (W. F. Magie)	22.20	
Expenses of Office of the Secretary	86.73	
Expenses of Office of the Treasurer	20.20	
Total		$1,286.49
Balance carried forward to 1905		1,625.12
		$2,911.61
Income:		
Interest on balance	$ 54.50	
Interest two life fees	3.50	
Annual dues, 232½	1,162.50	
Total	$1,219.50	$1,219.50
Outlays		1,264.29
Apparent annual deficit		$45.79

N. B. The apparent discrepancy between the number of dues paid and the subscriptions to the journals is due to paying back subscriptions and to present obligations.

WM. HALLOCK,
Treasurer.

THE RELATION BETWEEN RADIOACTIVITY AND COMPOSITION OF URANIUM COMPOUNDS.[1]

BY H. N. MCCOY.

I. To determine the *total* activity of unit mass of a uranium compound the absorption of the rays by the active substance itself must be taken into account. It has been found possible to determine the coefficients of absorption of the α rays for several pure uranium compounds. This was done by measuring, electrically, the activity of *uniform* films of the U compounds varying in thickness from 0.001 to 0.05 mm. The preparation of such films required special methods. The observed activity reached a maximum for the thickest films. If x is the ratio of the activity of any film to the maximum activity of a (thick) film of the same substance; then

$$\frac{\lambda}{d} = \frac{2.303 s}{w} \log \frac{1}{1 - x},$$

where s = area of film, w = weight, d = density, λ = absorption by unit thickness. Or $\lambda/d = k_2$ = absorption by unit weight on unit area. k_2 was found to be a constant for a given substance; but was different for different substances. The *total* activity of unit mass,

$$k_1 = 2k_2 a$$

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

a = *observed* maximum activity of unit area. If p = the proportion of U in a compound k_1/p = a constant ($\pm 1\%$) or the *total* activity is proportional to the U content.

II. The value of k_1/p for U ores was found to be a constant also. The latter constant was 4.17 times as great for the ores as for the *pure U* compounds. The excess activity of the ores is probably due to radium. The constancy of k_1/p for the ores shows the ratio of U to Ra to be a constant. This is the result to be expected if Ra is a decomposition product of U. The method above described allows a fairly accurate determination of the *total* activity to be made and is thus free from the objection that might be raised to the method first employed to test the theory of the origin of Ra.[1]

III. A method of preparing pure U_3O_8 to serve as a standard of radioactivity was described.

RELATION BETWEEN P.D. AND SPARK-LENGTH FOR SMALL VALUES OF THE LATTER.[2]

BY GLENN M. HOBBS.

USING one spherical and one plane electrode of brass, the curve expressing the relation between sparking potential (plotted as ordinates) and sparking distances (plotted as abscissæ) was as follows:

As distances diminished the P.D. was found to fall in a straight line curve until it reached 350 volts. The curve then ran parallel to the axis of abscissæ till the distance between the electrodes was about 2.5 μ when it dropped abruptly toward the origin. The sparking distance at which this latter change of direction occurred was found to vary with the material of which the electrodes were composed between the limits 1.5 μ and 3 μ.

THE INFLUENCE OF ELECTRODES UPON SPARK POTENTIALS.[2]

BY JOHN E. ALMY.

THE very considerable differences in the "cathode-fall" of various metals shown by the observations of Warburg, Mey and Skinner, suggested the possibility that spark potentials may depend upon the metal of the electrodes used. Various attempts to establish the truth of this inference have been without success.

Since hydrogen shows much greater differences in "cathode-fall" than other gases it seemed advisable to look for the effect of electrodes upon spark potentials in that gas. The "anode-fall" being sensibly constant for most metals, the differences to be expected would be essentially those due to difference of "cathode-falls."

[1] McCoy, Berichte d. Chem. Ges., July, 1904.

[2] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

The method of experiment used, shows only the variations of the difference between "cathode-fall," and "anode-fall" with the different metals; for if c and a equal the "cathode-," and the "anode-fall," respectively, the quantity measured in any case was a difference namely:

$$(c_1 - a_1) - (c_2 - a_2).$$
$$[i.e., c_1 + a_2 - (c_2 + a_1) = c_1 - a_1 - (c_2 - a_2)].$$

Two electrodes of different metals form a spark gap in hydrogen; the spark potential for a certain spark gap was measured first with one metal as negative electrode, then with the other metal negative, the difference between the spark potential in the two cases represents the difference:

$$(c_1 - a_1) - (c_2 - a_2).$$

Electrodes having radius of curvature of 10 cm. mounted in a tube filled with hydrogen at atmospheric pressure, were illuminated by an electric arc through a quartz window to eliminate "lag." A static machine and static electrometer, later a storage battery and Weston voltmeter were used to measure spark potentials.

A difference in the spark potential depending upon the material of the electrode was obtained, a difference independent of the spark length but depending to some extent upon the pressure of the gas, and upon the amount of moisture present. This difference gradually decreases with continued sparking, but returns to maximum value upon repolishing the electrodes, the decrease of the difference being, probably, due to the carrying over of the metal of one electrode to the surface of the opposite one.

The increments of the spark potential in volts in hydrogen with other metals as negative electrode, over that when aluminium forms the negative electrode are as follows:

Cathode Metal.	Pt	Cu	Ni	Fe	Zn
Mean with static machine.....	62	41	30	26	—
Increments with storage battery.....	53	33	—	19.5	16
Maximum increment with storage battery....	56	38	31	22	17

Minimum Spark Potentials. — Evidently the so-called minimum spark potentials, at least in so far as they refer to hydrogen, have definite significance only when the nature of electrodes used is specified. The minimum spark potentials for different combinations of electrodes in hydrogen, were determined, with gas pressure ca. 735 mm., at 20° C.

It is of interest to compare the values obtained with the "cathode-fall" of Warburg, and the "anode-fall" given by Skinner.

Minimum Spark Potential in Hydrogen (in Volts).

Metal.		Pt	Cu	Fe	Zn	Al
Cathode-fall in hydrogen		300	230	230	213	190
Anode-fall in hydrogen		18	19.5	20.3	20	20
Al	as cathode	230	230	249	235	237
	as anode	286	265	279	252	238
	difference	56	35	30	17	
Zn	as cathode	255	245	283		
	as anode	285	266	290		
	difference	30	21	7		
Fe	as cathode	268	280			
	as anode	286	295			
	difference	18	15			
Cu	as cathode	270				
	as anode	285				
	difference	15				

It is perhaps worth note, that the cathode effects are approximately additive, just as voltaic potentials, for example,

$$(\mathrm{Pt} - \mathrm{Cu}) + (\mathrm{Cu} - \mathrm{Fe}) + (\mathrm{Fe} - \mathrm{Zn}) + (\mathrm{Zn} - \mathrm{Al}) = 15 + 15 + 7 + 17 = 54 \text{ volts},$$

whereas,

$$\mathrm{Pt} - \mathrm{Al} = 56 \text{ volts}.$$

SOME ODDITIES IN LENSES.[1]

BY ALBERT B. PORTER.

1. *Convex Lens of Infinite Focal Length.*— The theory of thick lenses shows the focal length of a convex lens to be

$$f = \frac{n}{n-1} \cdot \frac{r^2}{2nr - (n-1)d},$$

where r is the radius of the curved faces, n, the refractive index, and d, the thickness of the lens. The focal length is positive or negative, *i. e.* the lens is convergent or divergent, according as d is less or greater than $2nr/(n-1)$. If $d = 2nr/(n-1)$, the focal length is infinite. Such a lens is neither divergent nor convergent, but gives inverted virtual images without magnification. With glass for which $n = 1.5$, this condition is secured by making $d = 6r$. Such a lens was shown.

2. *Convex Lens of Variable Thickness and Focal Length.*—By mounting two nearly hemispherical glass lenses at the ends of a telescopic tube

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

filled with a liquid of the same refractive index as the glass, a lens of variable thickness is obtained. By shortening or extending the tube the focal length may be made positive or negative at will. Such a lens was shown.

3. *Chromatic Lens.*—Hemispherical cavities are ground and polished in one side of each of two glass plates. The spherical cavity, which results when these plates are put face to face, is filled with Canada balsam thinned down with benzene and carbon bisulphide. If the liquid mixture has the same mean refractive index as the glass the resultant lens is strongly divergent for red light, strongly convergent for blue light, and acts like flat glass for some intermediate wave-length. Various focal lengths can be obtained by varying the composition of the mixture. When the radius of curvature is about three millimeters and the focal length is infinite for red light, it is less than 10 cm. for violet. These chromatic lenses are remarkably sensitive to temperature changes; a rise of less than 15° C. may cause a strongly convergent lens to become as strongly divergent. The color effects are very striking. These lenses are useful for demonstrating chromatic aberration. Examples of such lenses were shown.

4. *Chromatic Telescope.*—One of these chromatic lenses of moderately short focus may be used as the object glass of a small telescope. Such a chromatic telescope gives a sharp monochromatic image of the filament of an incandescent lamp. This image changes in color as the telescope is focussed, and is always surrounded by a halo of the complementary hue. The draw tube of such a telescope could be graduated for making rough measurements of wave-lengths in bright line spectra. Chromatic telescope shown.

5. *Lens Giving Rotating Image.*— When a cylindrical convex lens and cylindrical concave lens, of properly chosen focal lengths, are superposed with their axes crossed, the system gives an undistorted image of distant objects when it is held at a certain distance from the eye. If the lens system is rotated in its own plane, the image also rotates, but with an angular velocity twice as great. The image given by this system of lenses is peculiar in that it is a purely visual combination of two astigmatic images, one real the other virtual, one lying behind the lenses, the other in front. The image can neither be projected on a screen nor viewed through a telescope; it can been seen by the naked eye merely because of the short focus, and consequent depth of focus, of the eye. Rotating-image lens shown.

ON ABBE'S DIFFRACTION THEORY OF MICROSCOPIC VISION.[1]

BY ALBERT B. PORTER.

THE theory was stated in the following form. If a lens is to produce a truthful image of an illuminated object it must have an aperture sufficient to transmit the whole of the diffraction pattern produced by the object; if but part of this diffraction pattern is transmitted, the image will not truthfully represent the object but will correspond to another (virtual) object whose whole diffraction pattern is identical with that portion which passes through the lens; if the structure of the object is so fine, or the aperture of the lens so narrow, that no part of the diffraction pattern due to the structure is transmitted by the lens, then the structure will be invisible no matter what magnification be used.

It was shown that, in the case in which the object is a diffraction grating ruled with alternate opaque and transparent lines, the character of the image given by a lens of any aperture can be completely determined by means of Fourier's theorem. Curves were drawn showing the theoretical distribution of light in the images of variously ruled gratings formed by lenses of different apertures. These curves indicated that the images of certain gratings formed by lenses of certain apertures would contain false lines, in some cases dark, in others bright. These predictions were verified experimentally by using gratings ruled on smoked glass.

It was pointed out that, owing to these diffraction phenomena, a microscopic image may sometimes be profoundly modified by the presence of structure lying entirely beyond the focal plane. This was verified experimentally by means of two superposed transmission gratings whose ruled surfaces were two or three millimeters apart. A microscope was focussed on the upper surface and monochromatic illumination was used. With an objective of narrow aperture the image was normal in light of every wave-length but one; when this critical wave-length was used the image was completely obliterated. With an objective of wider aperture the image was again normal except in light of the critical wave-length; when illuminated by light of this color, the number of lines in the image doubled. These results were shown to be in exact agreement with theory.

It was shown that the theory applied to macroscopic as well as to microscopic vision, the apparent difference being merely due to the special methods of illumination commonly employed with the microscope. A method was described by which the experiments shown with Abbe's diffraction plate and a microscope can be repeated with a piece of wire gauze and the naked eye.

The equations which were used indicate that any opacity grating ruled

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

with n lines per unit length can be considered to be formed by the superposition, on an imperfectly transparent surface, of a series of simple gratings ruled with n, $2n$, $3n$, $4n$, etc., lines per unit length. The imperfectly transparent surface is responsible for the central image, while each of the simple gratings gives rise to the spectra of one order. The properties of simple gratings were discussed in connection with their microscopic images. It was shown that this analysis made it easy to design opacity gratings presenting any required anomaly. As an experimental verification of one deduction from the theory of simple gratings a photographic grating was made which, on account of the varying amount of blurring of the lines, showed spectra of several orders near one edge and spectra of but one order near the other. This grating was then used to secure a further verification of the diffraction theory of images.

The Relative Positions of the Arc and Spark Lines of the Spectra of Titanium and Zinc.[1]

By N. A. Kent.

THE variability or invariability of the wave-lengths of the lines of the spectra of arc and spark in the air at normal pressure is yet an unsettled question.

In 1902 Exner and Hascheck stated that some lines of the spark spectrum of titanium exhibit a considerable shift as compared with the same lines in the arc, a shift even as great as 0.13 t. m. in one instance.

In 1903 the author of the present paper made a careful experimental study of the question. No such large shift was discovered, but it was shown that in all probability the wave-lengths of certain lines of the Ti spark spectrum are sensitive to various conditions of the electric circuit — such as the amount of capacity, self-induction and ohmic resistance employed, and the presence or absence of an auxiliary spark-gap in series with that under investigation. The instrument used was a ten-foot Rowland grating. It seemed advisable to use greater dispersion. Hence the present work was undertaken. During its process Eder and Valenta have published a paper in which they state that neither in the case of pure zinc nor brass wire do the lines of the zinc spectrum studied by Exner and Hascheck show any shift. They attribute the results of these investigators to a photographic displacement of the center of gravity of the lines due to over-exposure — the lines in question being those which exhibit very strongly the phenomenon of unsymmetrical broadening; and they suggest also the possibility of a pseudo-shift due to poor focus. The conclusion drawn by Eder and Valenta is that, at minimum photographic exposure, the coincidence of arc and spark line is perfect. Moreover

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

Middlekauff has lately studied certain lines of the iron spectrum and finds no shifts under the conditions employed.

In the present investigation the aim of the author was to confirm his former results with titanium using greater dispersion and then to turn to the actual lines studied by Exner and Haschek, and Eder and Valenta.

The entire grating mount, camera-box included, is of metal (iron, steel and brass) and is supported by rubber disks on brick piers. The slit mechanism is in contact with the supporting channel beams only. The camera shutter is supported from the floor. Great care has been taken in regard to focus, temperature changes, accurate adjustment of the instrument, elimination of mechanical shifts, etc. The length of the lines of the grating (a 21-foot Rowland, concave) has been diminished by cutting down the vertical aperture to less than 2 cm. This process, together with stopping down the slit-length, so much reduces the astigmatism in the second spectrum that the tips of the spectral lines may be seen in the field of the filar micrometer used in measurement. We thus avoid a shift due to over exposure, for, by setting the cross-hair upon the tip of the spark image where it is just visible to the eye, we are certainly making use of minimum exposure conditions.

The results at present writing are as follows: Shifts occur under conditions which give great disruptiveness and involve a large amount of energy. These shifts approximate under certain conditions 0.05 t. m. for Ti λ 3900 and 0.07 for Zn (battery terminals) λ 4810. Brass wire under the same conditions gives a spectrum the lines of which show almost no shift.

Duplicate plates taken under similar conditions agree remarkably well, almost up to the average error of measurement of the same line on any one plate (approximately 0.005 t. m.). The results of the author's former investigation as far as touched upon at the present time are fully confirmed. It is difficult to see how we can avoid the conclusion that shifts do exist under certain conditions.

THE BLACK SPOT IN THIN LIQUID FILMS.[1]

BY E. S. JOHONNOTT.

IN some previous work on this subject (Phil. Mag., Vol. 47, p. 501) it was found that the black film, in general, consisted of two portions. That first formed varied in thickness between 40 $\mu\mu$ and 12 $\mu\mu$. This film was found to break into the second black of apparently constant thickness, 6 $\mu\mu$. The second black could only be produced by heating the first or exposing it to a drier atmosphere.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

It was recently discovered that great changes in character of the films could be produced by varying the pressure of the atmosphere surrounding the films. (1) A sudden increase in the pressure was accompanied by a rapid thinning, and (2) a sudden diminution in the pressure by a correspondingly rapid increase in thickness.

On subjecting the first black film to a sudden increase in pressure it was possible to convert it quickly into a second black; if then a sudden diminution in pressure followed, the second black became converted into a first black and this continuously into even the yellow of the first order.

The evident interpretation of these effects is that adiabatic compression is accompanied by an increased vapor pressure and evaporation from the surface of the film; while, on the other hand, adiabatic expansion causes a diminution in the vapor pressure and condensation on the film.

In view of these circumstances it was thought advisable to repeat the former work using a greater number of films and a different form of the interferometer.

The results obtained, for the first black film, confirm those previously taken. However, it was found that the second black, quite often, showed as high a value for the mean thickness as 9 $\mu\mu$, dropping very quickly to a mean value of about 6 $\mu\mu$. No further reduction in the value of the thickness could be produced by a sudden increase in the pressure, even when accompanied by a rapid rise in temperature.

Viewing the films with the microscope it was found possible, under proper conditions, to distinguish as many as five black films. These break, one into another, in the same manner as black films ordinarily are formed, each succeeding film being apparently thinner. The first three formed, however, are quite evanescent and seldom extend over an elevation greater than two or three millimeters. The fourth and fifth films formed are identical with what has been termed above the first and second black films, respectively.

It is hoped that it may be possible to obtain photographs of this condition as often times all five films are in the field of view at the same time.

Report of Progress in Ruling Diffraction Gratings.[1]

By A. A. Michelson.

THE principal elements upon which the operation of this ruling engine depend are the following:

1. The accuracy of the screw is tested by the interferometer.

2. The errors of run and the periodic errors thus found are corrected by grinding with pressure locally applied.

3. The residual errors are automatically corrected by compensating

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

devices which act on the worm which turns the screw; and the compensation is varied in such a way as to correct the varying errors in different parts of the screw.

4. The grating carriage floats on mercury so that only one tenth of the weight rests on the ways.

5. Only one of the three way-surfaces need be accurately straight, and this accuracy is secured by the use of the interferometer.

6. The ruling diamond is not pivoted but is attached to the ruling carriage by flexible copper strips.

7. The temperature is regulated by a thermostat.

The interferometer tests showed that the residual errors of the screw were of the order of a tenth of a light wave; and the resulting gratings (which may be fourteen inches in length) should have a resolving power of 500,000 in the third spectrum, and the ghosts should not be objectionable even in the fourth spectrum of a grating with 700 lines to the millimeter.

At present attention is given to the ruling carriage, the imperfections of which have prevented the attainment of this order of accuracy.

However, a grating of four inches has been ruled (which will be open to inspection) which shows everything which can be seen with the six-inch Rowland grating.

It would appear from past experience that the efficiency of gratings ruled by the present methods does not increase as rapidly as the length of the ruled surfaces — or to put it in another way, it is more difficult to make a long screw than a short one of the same degree of accuracy; so that if the hope of a grating with a resolving power of a million is ever to be realized (experiments on visibility, and also results obtained with the echelon show structure which would require this resolving power) it will probably be by some other plan.

Two such plans have been devised, one of which is thus far only on paper. The machine which embodies the second is near completion, and will be tested in a few weeks.

The first plan contemplates the use of four (or more) screws, whose motions by a simple system of levers are communicated in succession to the grating carriage, thus diminishing in the same proportion the unavoidable errors of each.

The second plan dispenses entirely with screws. The motion of the grating is affected by the rise of mercury in four accurately ground cylinders. The grating support floats on the mercury and is otherwise practically free, so that during the motion it remains parallel to itself and requires no guiding ways. The level of the float is raised by dropping a fixed quantity of mercury (by means of a valve of special construction) into a tube which communicates with the cylinders. Some preliminary

experiments with the mercury valve showed that the successive weighings of twenty drops differed from the mean by quantities of the order of one hundred thousandth.

Use of the Concave Mirror with Diffraction Gratings.[1]

By A. A. Michelson.

THERE seems to be an impression that the use of the concave mirror with diffraction gratings is impracticable on account of the aberration resulting from the fact that the central ray cannot coincide with the axis of the mirror.

In the disposition actually employed for testing gratings no such difficulty arises, and the images obtained are practically perfect.

The light from the slit is totally reflected by a prism in the eyepiece and proceeds to the concave mirror (ten inches diameter and ten feet focal length) which renders the pencil parallel. The parallel beam falls on a grating which is immediately in front of and just below the eyepiece. The diffracted parallel beam is again returned to the concave mirror whence it proceeds to form the spectral image in the focus of the eyepiece.

Reciprocal Diffraction Phenomena.[1]

By A. A. Michelson.

IT is shown theoretically that if V is the motion at the surface of the light-wave which coincides with the diffracting screen of a telescope, and if W is the resulting diffraction pattern at the focus, then, reciprocally, if W is the motion at the diffracting screen the resulting diffraction pattern will be V.

This is illustrated experimentally.

The Dielectric Strength of Double-refracting Crystals.

By John E. Almy.

THE dielectric strength of various solid dielectrics seems to bear no simple relation to any of the other physical properties of those substances, with the possible exception that in substances of like character — different kinds of glass, for example — the dielectric strength is greatest in those having the least electrical conductivity.

The dielectric strength of crystals was measured to test the existence of a possible relation between dielectric strength and the optical properties of such media.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

Plates of quartz, selenite, aragonite, and Iceland spar were used, the dielectric strength being determined by the method previously used (cf. Ann. der Phys., Bd. 1, Ser. IV., p. 508) by the author. The plates of quartz were cut normal, and parallel, respectively, to the optic axis of the crystal; plates of selenite obtained by simple cleavage; plates of aragonite were cut parallel to the plane of the optic axes, and normal to the bisector of the acute angle between the axes, respectively, and plates of spar cut normal to the optic axis, parallel to the axis, and parallel to the faces of the crystal, respectively.

In the case of quartz the dielectric strength is clearly greater (as is also the electrical resistance at 300° C.) in the plates cut parallel to the optic axis. In none of the other crystals is there a clearly shown difference in the dielectric strength depending upon the direction of the discharge.

The observations are as follows:

Selenite:

Thickness of plate (cm.):	.01	.009	.92	.02	.038	.04	.044	.05	.053
Spark potential (C.G.S.):	38	30	59	68	107	102	108	126	135
" " (calc.):	33	31	56	56	97.4	102	111	125	132

Quartz (plates cut parallel to the optic axis):

Thickness (cm.):	.006	.016	.017	.030	.032	.037	.020
Potential (C.G.S.):	40	96	90	117	120	125	102
" (calc.):	75	91.4	93	114.5	118	126	98

Quartz (plates cut normal to the optic axis):

Thickness:	.0045	.008	.015	.028	.030	.039	.020
Potential:	30	44	59	87	90	117	76
" (calc.):	33	42	58.5	89.7	93	115.6	71

Aragonite (plates cut parallel to plane of axes):

Thickness:	.07	.075	.095	.10	.115
Potential:	76	72	109	81	111
" (calc.):	76	79	93	96	106

Aragonite (plates cut normal to plane of axes):

Thickness:	.035	.043	.055	.060	.075	.080	.080	.097	.105
V (observed):	51	62	64	67	85	81	87	91	85
V (calc.):	53	58	66	696	79.5	83	83	94	99

Iceland Spar:

	Plates cut normal to axis:						Plates parallel to axis:			
T:	.045	.045	.071	.070	.103	.109	.045	.065	.066	.070
V:	87	102	100	120	125	130	73	95	113	104

Plates parallel to faces of crystal:

T:	.046	.070	.082	.087
V:	103	111	120	125

For each substance, excepting possibly the Iceland spar, the spark potential, V, may be expressed as a linear function of the thickness of plate, T, that is—

$V = aT + b$, where a and b are constants, characteristic of the substance. The values of these constants obtained, together with other constants, are as follows:

	a	b	μ (for D Line.)	Electr. Conductivity 100°.
Mica	18800	10	1.57–1.61	$27° 10^{-21}$
Quartz { cut II to axis	1650	65	1.544 (μ ordinary)	
Quartz { " I " "	2400	22.5	1.544–1.°553	$11\times10_{-17}$
Selenite	2300	10	1.520–1.530	
Aragonite (averages)	−660	30	1.53–1.685	
Iceland spar (averages)	−635	65	1.48–1.65	2.40×10^{-18}

On the Comparison of Mutual Inductances.[1]

By A. H. Taylor.

THE same alternating current is sent through the primaries of the two pairs of coils, and across the secondary giving the higher E.M.F. is placed a very high resistance—5,000 to 100,000 ohms. If this resistance be made up of two parts, r_1 and r_2, and M_1 is the coefficient of mutual inductance of this pair of coils, then the E.M.F. over r_1 may be made to balance the E.M.F. of the secondary of the second pair of coils. Or,

$$\frac{M_1(r_1)}{r_1 + r_2} = M_2,$$

where M_2 is the coefficient of the second coil. Balance can be obtained with a telephone, but a higher order of accuracy may be attained with an alternating current galvanometer. For instance, for a mutual inductance of .035 millihenry the order of precision is about 0.1 per cent., while for as small a mutual inductance as .002 millihenry (the Tesla coil of a wireless telegraph sender, primary four turns, secondary two hundred turns) consecutive settings with different resistances for r_1 and r_2 agree to about 2.5 per cent. For higher inductances, of the order of a few millihenries, the order of precision is very nearly that of the resistance boxes used, *i. e.*, .01 per cent.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

ON THE POSSIBLE VARIATION OF INDUCTANCE STANDARDS WITH TEMPERATURE.[1]

BY A. H. TAYLOR.

THE standard variable inductance examined was of the familiar Ayrton Perry type, consisting of two coils wound on portions of concentric spherical mahogany frames.

It was thought that temperature variations might produce unequal expansions in different portions of the wooden frames and so alter the configuration of the coils as to produce an appreciable difference between inductance values when used at different temperatures.

The inductance L in series with a capacity C was placed in one arm of a bridge whose other three arms were ohmic resistances. The inductance had a resistance r_0 and was shunted with a resistance R, while the capacity was shunted with a resistance r, very nearly equal to R. The two proportional arms of the bridge were made equal and R_1 was the resistance required to balance the arm containing L and C for steady currents. Then an alternating current at 60 cycles was applied to the bridge and balance obtained with an alternating current galvanometer. The inductance L is given in terms of the capacity as closely as the resistances may be known by the equation

$$L' = \frac{r^2 C (R_1 + r_0)^2}{r + R - R_1}$$

With high bridge resistances, 110 volts A.C. across the bridge, and fixed R, r_0, R_1, r, and C, a change of $\frac{1}{30000}$ in the inductance could be noted by placing on the rotating top of L a mirror to be used with a telescope and scale two meters distant. The inductance L was placed in a wooden box, balance obtained, and the scale reading taken. The temperature of the box was raised 10° C., the bridge balanced again and a new scale reading taken. Change in r_0 due to this change in temperature was compensated. The standard was tested in three positions of the rotating coil, eight hours being allowed for the standard to assume the temperature of the box.

The results were in all cases practically negative. At least it is safe to say that for this standard, as probably for others of the same type, the variation of inductance with temperature is less than $\frac{1}{40000}$ per degree centigrade.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

[2] A. Trowbridge, On the Differential Transformer, PHYS. REV., February, 1905.

On the Variation of a Capacity with Temperature.[1]

By E. M. Terry.

USE of the alternating current galvanometer in high precision measurements of inductance and capacity was first made by Stroud and Oates.[2] The instrument is of the D'Arsonval type, except that the field is built up of laminations of soft iron and wound to be used on the 110 volt alternating circuit.

The difficulty in manipulation lies in the fact that a closed coil of wire suspended in an alternating magnetic field takes up a position of great stability in the position in which its axis is at right angles to the field. Stroud and Oates overcame this by placing upon the coil another closed coil at right angles.

Since, however, a lagging current in the coil makes it take a position with its axis at right angles to the field, while a leading current, one with it parallel to the field, the author has found that by properly adjusting the conductivity and capacity across the coil, it may be made practically astatic.

Two capacities were compared by the bridge method using the alternating current galvanometer, with a drop of 220 volts across the bridge. The ratio of the capacities could be determined to .01 per cent., which was the limit to which the resistances could be depended upon. However, by keeping the resistances practically constant and shunting across a small part of one of them, a change in one of the capacities of the order of 1 part in 100,000 could be easily detected.

The temperature coefficient of each part of a subdivided condenser was obtained working between 16° C. and 33° C. It was found to be negative and to vary between .01 per cent. and .03 per cent. per degree for the different parts.

Infra-Red Emission Spectra of Vacuum Tubes.[1]

By W. W. Coblentz.

HERETOFORE the dispersed radiation from a vacuum tube has never been extensively investigated. The only exception to this statement is the work of Runge and Paschen[3] who, using a bolometer, examined the infra-red of helium (Cleveite gas) for spectral series lines, and

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society April 21, 1905.

[2] Phil. Mag., Dec., 1903.

[3] Runge and Paschen, Astrophys. Jour., 3, p. 4, 1896.

the work of Drew[1] who using the writer's apparatus examined the emission spectrum of air incidentally with his efficiency investigation.

Ångström[2] measured the total radiation from vacuum tubes and remarks that to do so is a difficult matter, so that after dispersing the radiation the task is well nigh impossible. He found that the total radiation *increases*, while the luminous radiation *decreases*, with *increase* in pressure of the gas, and concluded that there are two kinds of radiation present during the electrical discharge, viz., "regular" and "irregular" (luminescence). After noticing the present results it will become apparent that his predictions are in remarkably close agreement with observed facts. Ferry[3] found that for certain lines of *N* and *H*, which he studied, at constant pressure the intensity is proportional to the current and with constant current the intensity increases with decrease in pressure. Langenbach[4] obtained similar results, except that with constant current the intensity passes through a maximum for decrease in pressure of the gas.

All the infra-red lines predicted by our spectral series formulæ end in the short wave-lengths just beyond the red. The present investigation deals with the question of the presence of lines beyond this point. At the December meeting of the Physical Society attention was called to the fact that no lines were found beyond 2 μ and that, for the metals in the arc, the oxides emit sufficient radiation to obliterate any weak lines that may be situated beyond this point. The vacuum tube radiation does not contain that of the oxides, hence adapts itself readily to this work provided one has a sensitive apparatus to measure the changes in temperature. The radiometer used in the preceding work was remodeled and made unusually sensitive. In fact it is the most sensitive radiometer yet constructed, being 52 times that of the Boys' radiomicrometer. The vacuum tube consisted of a glass tube 1 cm. internal diameter and 15 cm. long, the ends of which were enlarged sufficiently to contain cylindrical electrodes 3 cm. in diameter. The radiation passed axially through one of these electrodes, through a rock salt window, into the spectrometer slit of 0.8 cm. length. The following gases were examined: CO, CO_2, NH_3, H, O, N and the vapors of C_2H_5OH and H_2O. They were introduced from the gas-pipettes through a barometric column of mercury.

In the preliminary work, an emission band was found at 4.75 μ for all gases except H and H_2O. After eliminating all traces of CO_2, this band was not found in any gas except C_2H_5OH, CO_2 and CO. Since the radiation from this band is much more intense for CO than for CO_2 it is quite

[1] Drew, PHYS. REV., 17, p. 321, 1903.
[2] Ångström, Wied. Ann., 48, p. 493, 1893.
[3] Ferry, PHYS. REV., 7, p. 1, 1898.
[4] Langenbach, Ann. der Phys., 10, p. 789, 1903.

probable that it is due to the former gas. The CO_2 dissociates at high temperatures and since, the "electrical temperature" is high[1] and since the pressure is low, one would expect to find the CO_2 almost entirely dissociated. The absorption band of CO_2 occurs at $4.28\,\mu$ and that of CO at $4.59\,\mu$. Paschen found that the CO_2 emission band shifts toward the CO band with rise in temperature, being at $4.4\,\mu$ in the bunsen flame. One reason for undertaking the vacuum tube radiation was to test the question whether this shifting is due to dissociation. For the vapors of Na, K and Li in the arc, a band was found at $4.53\,\mu$.

Of the gases studied, only H and N have appreciable radiation near the visible spectrum. For N the bands are very intense (deflections as great as 20 cm.) and the important maxima at .75, .90 and $1.06\,\mu$ agree with those found in air, by Drew. In air these bands are very weak.

The bands at .53, .66, .75, .90, 1.06 and $4.75\,\mu$ were examined for constant current and varying pressures, and vice versa. The current varied from .01 to .025 amperes. The band at $4.75\,\mu$ behaves in an entirely different manner from all the rest. Its intensity increases with increasing pressure (for constant current) but never reaches a maximum, becoming quite asymptotic at 5 to 6 mm. pressure. On the other hand, the other bands increase in intensity with increase in pressure, become a maximum at about 2 mm. pressure, then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum. All lines increase in intensity with increase in current as found in the visible spectrum. Condensers in parallel had only a slight effect in increasing the intensity due to an increase in the current through the tube.

The whole shows that the bands near the visible spectrum are related to the visible bands of nitrogen and hydrogen, while the $4.75\,\mu$ band is of an entirely different type.

The following tentative explanation is offered for these two very different kinds of radiation. It seems the most plausible one of a number that present themselves. Consider the lines near, and in, the visible spectrum. At higher pressures the electrons will not attain a high speed and their freedom of motion will be limited; at a lower pressure their freedom of motion will be greater, the number of impacts will be more frequent and the "electrical temperature," which is proportional to the mean square of the ionic speeds, will attain a maximum. At a still lower pressure, due to the scarcity of ions, the impacts decrease in number, in a given time, and the electrical temperature decreases.

On the other hand, the band at $4.75\,\mu$ appears to be due to a thermal radiation, excited by the impact of electrons with the gas molecules

[1] Stark, Elektricität in Gasen, from consideration of the kinetic energy of the electron, computes an electrical temperature of some 6000°.

which will grow warmer and in colliding with other molecules, on account of their temperature, will emit heat waves. With increase in pressure (*i. e.*, number of gas molecules) the number of collisions will increase, the intensity of radiation will increase, but will not pass through a maximum as is true of the other bands.

Whether this band is due to a thermal or an electrical excitation of the molecules is not known. Its behavior can be explained on either of these two assumptions. There are several reasons for believing that the radiation is thermal, although we know nothing about the temperature of the tube. First, the gas must be hotter than the tube (Warburg, also Drew, *loc. cit.*), for, during the passage of the current the radiation tangential to the axis of the tube is probably different from the longitudinal, and the cell walls assume the temperature of the gas only after the current has passed for some time. Second, the distribution of the temperature is very different for different pressures. At a high pressure the constricted portion of the vacuum tube is the hotter, while at low pressures it is quite cool, and the region surrounding the electrodes is the hotter. Third, the emission increases with pressure (equivalent to an increase in thickness of the emitting layer) and approaches a limiting value just as in the case of a black body. Paschen[1] has found for CO_2 in a brass tube heated by a bunsen burner, that a column 7 cm. long emitted and absorbed the band just as strong as a column 33 cm. long, *i. e.*, it behaves like a column of infinite thickness; it radiates and absorbs like a black body. In the present work a tube of CO_2, 1 cm. diam., 15 cm. long, heated to about 100° gave a deflection beyond the end of the scale for *all* pressures, showing that the black body radiation is the stronger. This would indicate that if the 4.75 μ band were "irregular" (call it electrothermalescence) rather than thermal then its intensity ought to be greater than that of the black body (the tube of CO_2, heated externally) at the same temperature.

In the present work we cannot find the absorption, and only that part of the Kirchhoff law which refers to the emission can be considered. Here, for a pressure of 5 to 6 mm. the CO_2 emission already approaches a fairly constant value. This shows that the radiation of a layer of thickness dx, situated at the end of the tube farthest from the spectrometer slit, is almost entirely absorbed by the intervening layers before it passes into the spectrometer slit. The emission band of CO at 4.75 μ is more intense than that of the hot tube, except at the lowest pressures when the hot cell gave very large deflections, which at first thought would make it appear as though the band were due to electrical rather than to thermal excitation. From the work of Warburg and of Drew the temperature of the axis of the tube is at least 250° C.

[1] Paschen, Wied. Ann., 51, p. 1, 1894.

The question of the dissociation of CO_2 is still more difficult to consider. Beginning with CO_2 at a pressure of 1.5 mm. and adding oxygen in small quantities until the pressure was 4 mm. no change in intensity of the CO_2 band was observed, except possibly at the very first. This, however, proves nothing, since the slight amount of CO formed on adding oxygen would hardly be sufficient to increase the radiometer deflections more than the variations in the readings for the original CO_2.

In other words, we must begin with a larger quantity of CO_2, and add the O before passing the discharge. Then compare the radiometer deflection for the mixture with that obtained for CO_2, at the same pressure. This is a problem that needs further attention.

The *decrease* in infra-red radiation and the simultaneous *increase* in the visible radiation, with *decrease* in pressure, explains the rise in efficiency of vacuum tubes.

In conclusion it does not seem out of place to emphasize the fact that no lines have been found beyond 2 μ (except the 4.75 μ band which does not behave like the visible lines), as already noticed at the December meeting.

Diffraction Fringes from Electric Discharges and from Fluid Streams.[1]

By Arthur L. Foley and Joseph H. Haseman.

An open-ended rectangular wood box or tube about .15 x .15 x 4 m. was arranged to telescope into a similar box, both painted dead black. At one end of the tube was placed a diaphragm with apertures of various sizes, the one generally used being .01 cm. in diameter. The other end of the box was provided with a camera back and plate-holder. The aperture was illuminated by an arc lamp, a prism being used to get approximately monochromatic light. The needles, etc., were placed near the end of the smaller tube and their distance from the plate varied by telescoping the tubes.

The needles were fixed with their axes parallel and with their points toward one another and from .5 to 3 cm. apart. They were insulated and connected to the terminals of a Wimshurst machine driven at any desired speed by means of a motor and reducing gear.

The usual diffraction fringes were obtained when the needles were uncharged. When charged there were fairly distinct fringes about the path of the discharge between the two points. Fringes were obtained

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society on April 21, 1905.

from both visible and invisible brush discharges, and from rapid spark discharges.

The needles were replaced by a glass tube with the end drawn to a capillary, and various gases and vapors were forced through the tube. CO_2, ether, bromine, illuminating gas, H, and hot air streams gave definite diffraction fringes, both inside and outside the geometrical shadow. Calculation from measurements of the width of the fringes shows that such streams act as if they had very definite edges or boundaries, even at a distance of several cm. from the orifice.

The effect of ball and point discharges, of high and low potentials, of discharging in different gases, and of varying the density, pressure, and temperature of the gas and vapor streams, will be published soon. Work on liquid streams is now in progress. An attempt will be made to apply the method to the study of other types of fluid motion.

EXPERIMENTS ON THE FLOW OF ELECTRICITY IN METALS UNDER CHANGES OF PRESSURE.[1]

BY C. B. THWING.

A BAR of the metal, *A*, is connected by a fine wire, *a*, of the same metal to one pair of quadrants of a sensitive electrometer. *A* is enclosed in a straw jacket and heated to 100°, while *a* is at the temperature of the room. When *A* is heated the electrometer is charged negatively. When *A* is cooled the electrometer is charged positively.

If *A* is enclosed in a stout tube of steel, insulated in oil, and hydrostatic pressure applied, the charge obtained is + and for pressures of 10–20 atmospheres, is in the case of some metals as much as .1 volt.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society on April 21, 1905.

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ERRATA.

P. 269, line 22. For "0 mm." read 50 mm.

Note also corrections to the article by M. F. McDowell on Circular Dichroism in Natural Rotary Solutions. In the bound volume these corrections should appear opposite p. 170.

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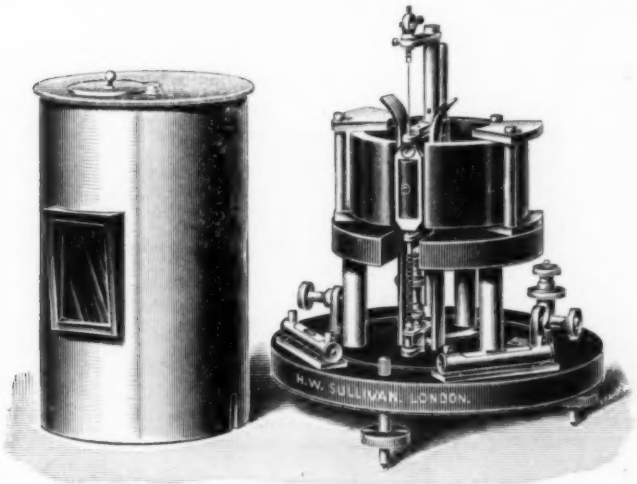

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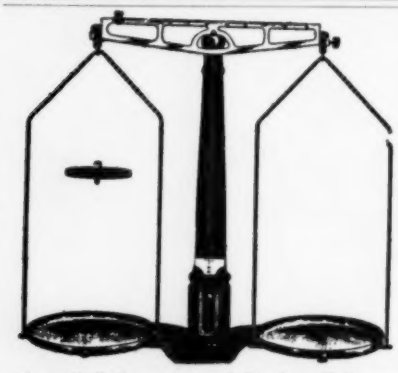

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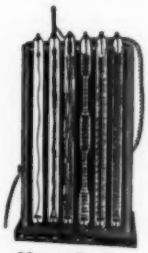

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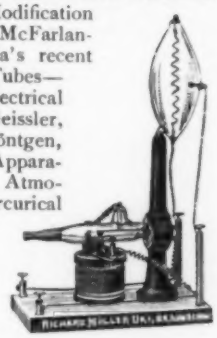

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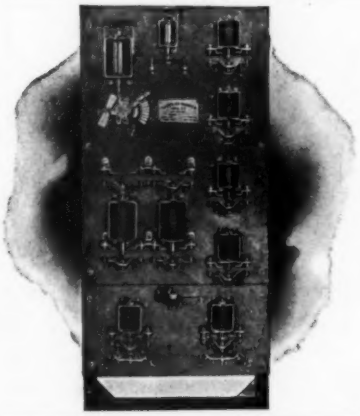

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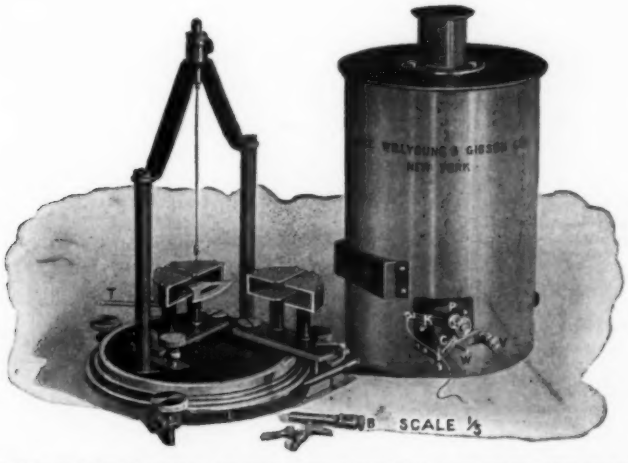

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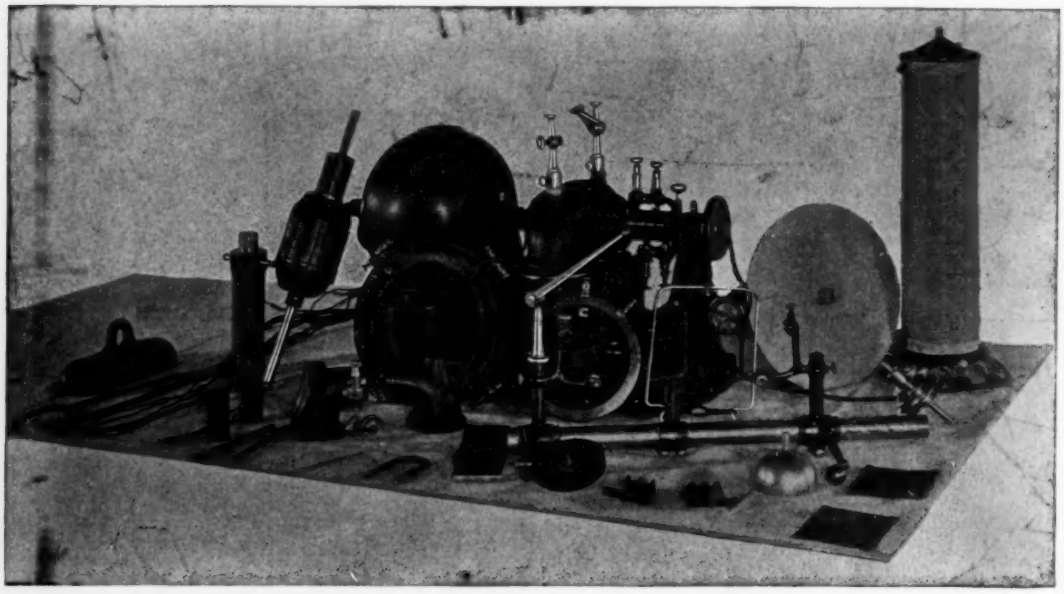

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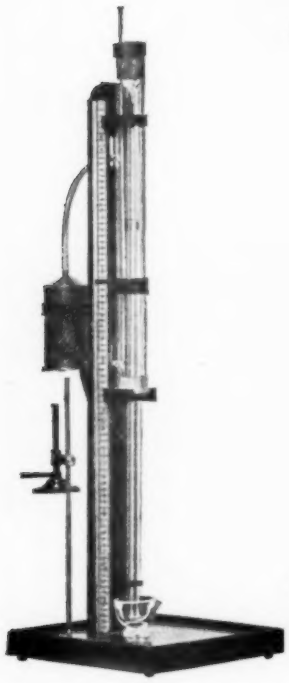

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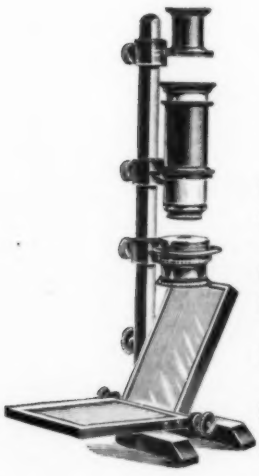

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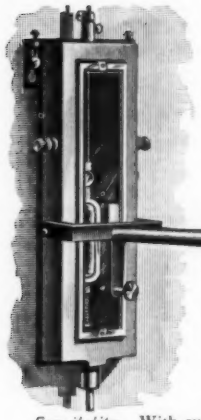

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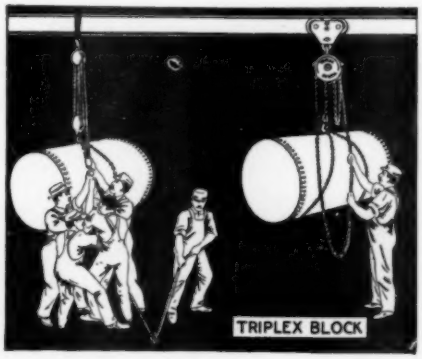

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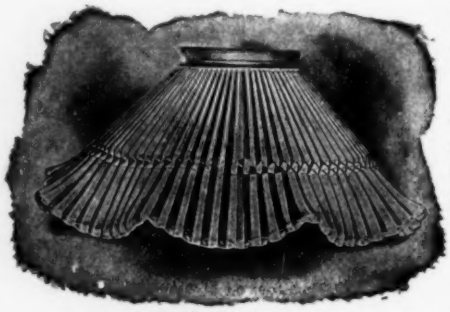

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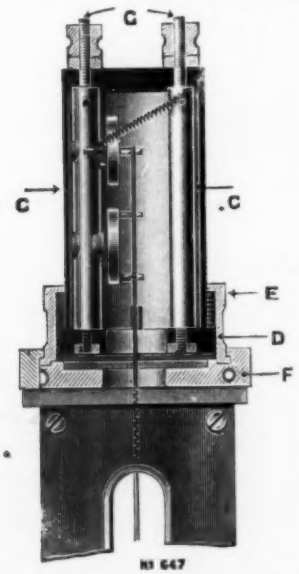

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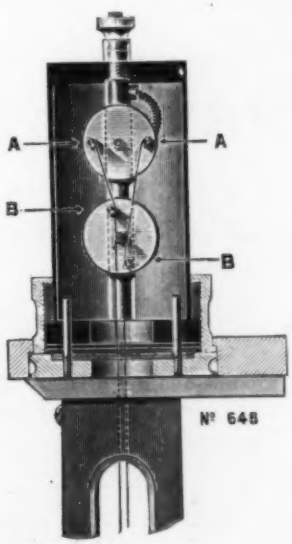

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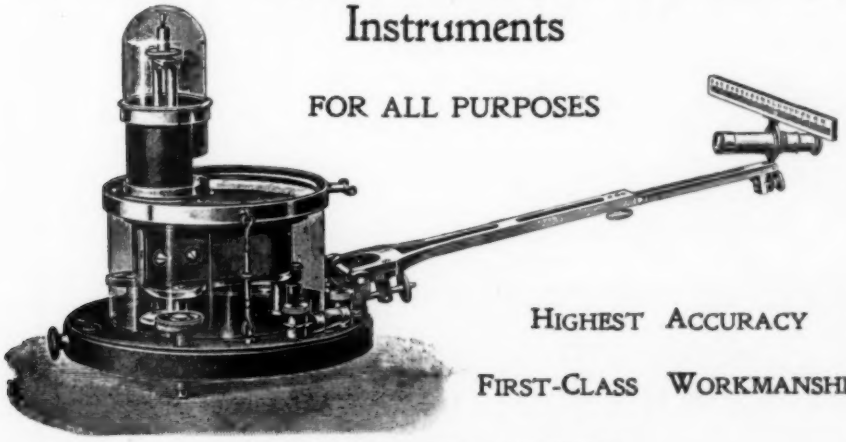

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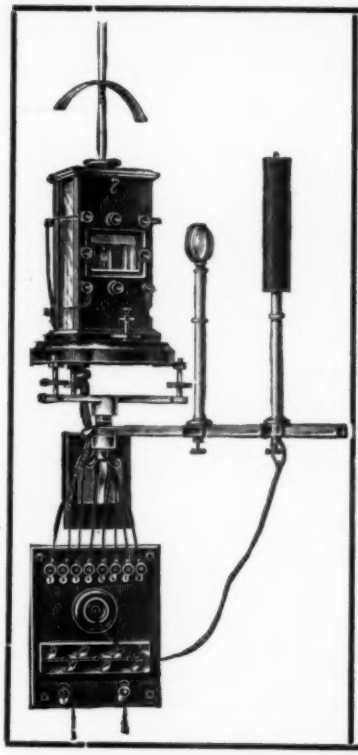

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